- **COMMON NAME**
- **NOMENCLATURE**
- **GOC & ACIDITY & BASICITY**
- **STOICHIOMETRY - II**

Corporate Head Office

394 - Rajeev Gandhi Nagar Kota, (Raj.)

Ph. No. : 08003899588, 0744-2209671

IVRS No : 0744-2439051, 52, 53,

www. motioniitjee.com , info@motioniitjee.com

MOTION
Nurturing potential through education

CHEMISTRY

TARGET (JEE MAIN + JEE ADVANCED)

THEORY AND EXERCISE BOOKLET

CONTENTS

JEE SYLLABUS

- **NOMENCLATURE**

JEE - ADVANCED

Concepts: Hybridisation of carbon; Sigma and pi-bonds; Shapes of simple organic molecules;IUPAC nomenclature of simple organic compounds (only hydrocarbons, mono-functional and bi-functional compounds)

- **GOC & ACIDITY & BASICITY**

JEE - ADVANCED

Inductive and resonance effects on acidity and basicity of organic acids and bases; Polarity and inductive effects in alkyl halides; Reactive intermediates produced during homolytic and heterolytic bond cleavage; Formation, structure and stability of carbocations, carbanions and free radicals.

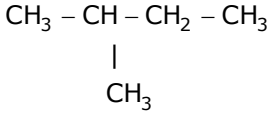
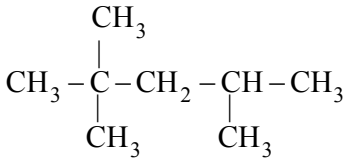
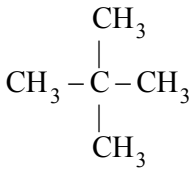
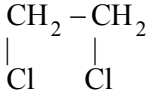
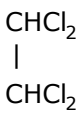
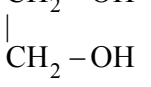
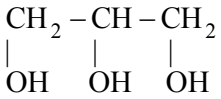
- **STOICHIOMETRY - II**

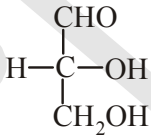
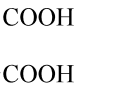
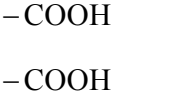
JEE - ADVANCED

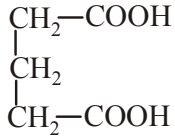
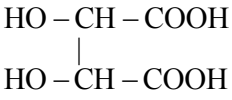
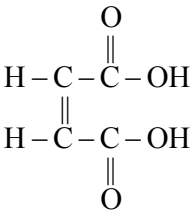
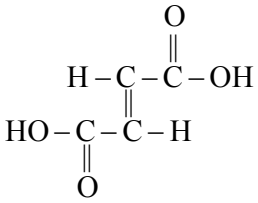
Calculations (based on mole concept) involving common oxidation-reduction, neutralisation, and displacement reactions; Concentration in terms of mole fraction, molarity, molality and normality.

COMMON NAME

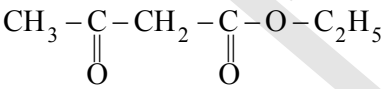
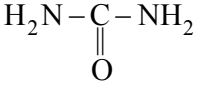
ESSENTIAL

S.No.	Compound	Common Name
	Group A: → ALKANES	
1		Isopentane
2		Isooctane
3		Neopentane
	Group B:→ ALKENES	
4	$CH_2=C=CH_2$	Allene
	Group C:→ ALKYL HALIDE	
5	CH_3CHCl_2	Ethylidene Chloride (A gem dihalide)
6		Ethylene Dichloride (A Vinyl dihalide)
7		Westron (Solvent)
8	$ClCH=CCl_2$	Westrosol or Triclean (Solvent)
	Group D:→ALCOHOL	
9		Glycol or Ethylene Glycol
10		Glycerol

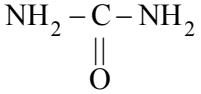
S.No.	Compound	Common Name
11	$CH_2=CH-CH_2-OH$	Allyl Alcohol
12	$CH_2=CH-OH$	Vinyl Alcohol
	Group E:→ETHER	
13	$C_6H_5-O-CH_3$	Anisole (Methyl Phenyl Ether)
	Group F:→ ALDEHYDE	
14	$CH_3CH=CH-CHO$	Crotonaldehyde
15	$CH_2=CH-CHO$	Acraldehyde or Acrolein
16		Glyoxal
17		Glyceraldehyde
	Group G:→KETONE	
18	CH_3COCH_3	Acetone
	Group H:→CARBOXYLIC ACID	
19		Malic acid
20		Lactic Acid (In milk)
21	NH_2-CH_2-COOH	Glycine (Amino Acetic Acid)
22	$HO\ CH_2\ COOH$	Glycolic Acid
23		Malonic acid
24		Succinic acid

S.No.	Compound	Common Name
25		Glutaric acid
26	$COOH–(CH_2)_4–COOH$	Adipic Acid
27		Tartaric acid
28		Maleic acid
29		Fumaric acid

Group I:→ACID DERIVATIVES

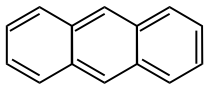
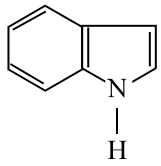
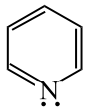
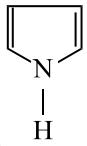
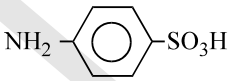
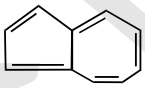
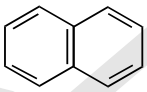
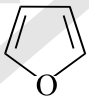
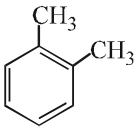
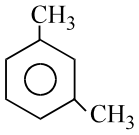
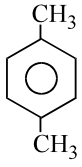
30		Aceto Acetic Ester **(AAE)** or Ethyl Aceto Acetate
31		Urea

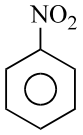
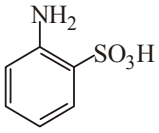
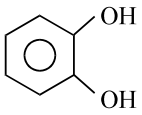
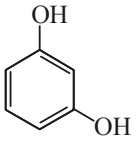
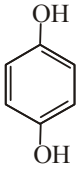
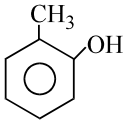
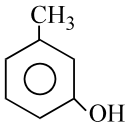
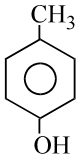
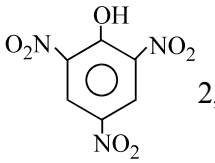
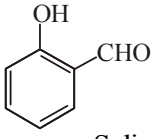
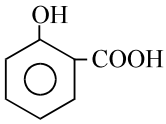
Group J:→N–DERIVATIVES

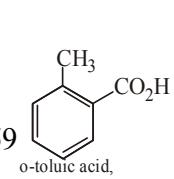
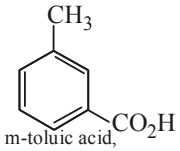
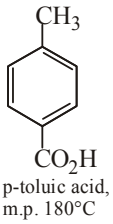
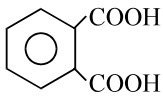
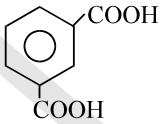
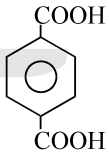
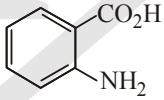
32	$CH_2=CH–C\equiv N$	Vinyl Cyanide or Acrylo Nitrile
33		Urea
34		Guanidine

S.No.	Compound	Common Name

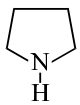
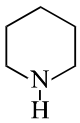
Group K:→AROMATIC COMPOUNDS

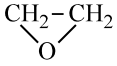
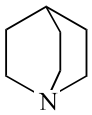
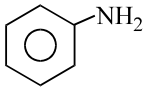
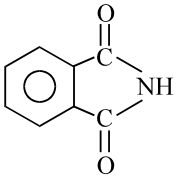
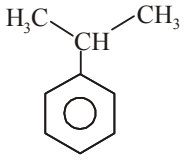
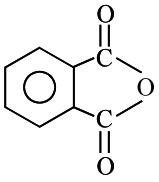
35		Anthracene
36		Indol
37		Pyridine (Py)
38		Thiophene
39		Pyrrole
40		Sulphanilic acid
41		Azulene
42		Napthalene
43		Furan
44		o–xylene
45		m-xylene
46		p-xylene

S.No.	Compound	Common Name
47		Nitrobenzene (oil of mirbane)
48		Orthanilic Acid
49		Catechol
50		Resorcinol
51		Quinol
52		o-Cresol
53		m-Cresol
54		p-Cresol
55		2,4,6 Trinitrophenol or Picric acid
56		Salicylaldehyde(o-hydroxybenzaldehyde)
57		Salicylic acid

S.No.	Compound	Common Name
58	$C_6H_5CO_3H$	Perbenzoic acid
59	  	Toluic acids
60		Phthalic acid
61		Isophthalic acid
62		Terephthalic acid
63		Anthranilic acid (o-aminobenzoic acid)
64	C_6H_5CHO	Benzaldehyde

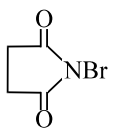
Group L:→ HETROCYCLIC COMPOUNDS

65		Pyrrolidine
66		Piperidine

S.No.	Compound	Common Name
67		Tetrahydrofuran (THF)
68		Oxirane or Ethylene Oxide or Oxo Cyclo Propane
69		Quinuclidine
70		Aniline
71		Phthalimide
72		Cumene
73	Ph–CH=CH–CHO	Cinnamaldehyde
74		Phthalic anhydride

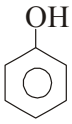
SOME REAGENTS

75	Grignard's reagent	RMgX
76	NBS	N-Bromosuccinimide



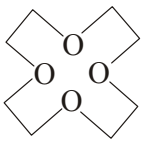
S.No.	Compound	Common Name

POLAR PROTIC SOLVENTS

77	H–O–H	Water
78	R–O–H	Alcohol
79		Phenol
80	$CH_3–\underset{\underset{O}{\|}}{C}–OH$	Acetic acid
81	HF	Hydrogen Fluoride
82	NH_3	Ammonia

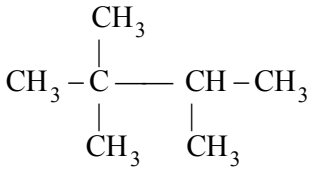
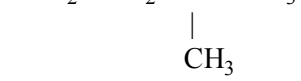
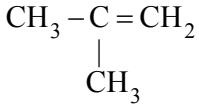
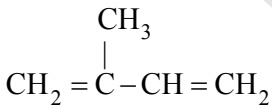
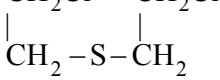
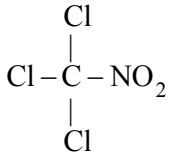
POLAR APROTIC SOLVENTS

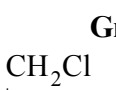
83	DMS	Dimethyl sulphide $CH_3–S–CH_3$
84	DMSO	Dimethyl sulphoxide $Me_2S=O$
85	HMPT or HMPTA	Hexamethylphosphoramide $O=P–(NMe_2)_3$
86	DMF	Dimethyl formamide $H–\underset{\underset{O}{\|}}{C}–NMe_2$
87	Crown ethers	Cyclic polyethers



(12 – C – 4)

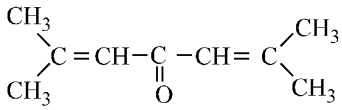
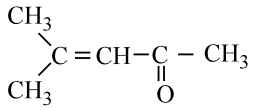
DESIRABLE

S.No.	Compound	Common Name
	Group A: → ALKANES	
1		Triptane
2		Isopentyl Group
	Group B:→ ALKENES	
3	$CH_3–CH_2–CH=CH_2$	α–Butylene
4	$CH_3–CH=CH–CH_3$	β–Butylene
5		Iso Butylene
6		Isoprene
	Group C:→ ALKYNES	
7	$HC\equiv CH$	Purified Acetylene or Norcelyne
8	$CH_2=CH–C\equiv CH$	Vinyl Acetylene
9	$CH_3–C\equiv CH$	Allylene
	Group D:→ ALKYL HALIDE	
10		Mustard Gas (Poisonous; used in war)
11	$Cl_2C=CCl_2$	Tetraclean or Perclean
12		Chloropicrin (tear gas)

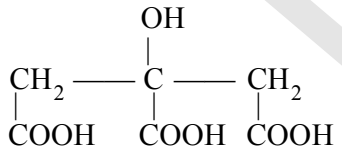
S.No.	Compound	Common Name
13		Chloretone
14		Chloroprene
15		Lewisite
	Group E:→ALCOHOL	
16	$CH\equiv C–CH_2–OH$	Propargyl Alcohol
17		Pinacol
	Group F:→ETHER	
18	$C_6H_5–O–C_2H_5$	Phenetole (Ethyl Phenyl Ether)
19	$CH_3CH(OCH_3)_2$	Methylal
	Group G:→ALDEHYDE	
20		Glyoxalic acid
21		Pivaldehyde
22	$(CH_3)_2CHCHO$	Isobutyraldehyde

S.No.	Compound	Common Name
23	$CH_3-C(=O)-C(=O)-CH_3$	Dimethyl Glyoxal
24	$CH_3-C(=O)-C(=O)-H$	Methyl Glyoxal or Pyruv aldehyde

Group H:→KETONE

25		Phorone
26		Mesityl Oxide
27	$H_2C=C=O$	Ketene

Group I:→CARBOXYLIC ACID

28	$CH_3-(CH_2)_3-COOH$	Valeric Acid (n–Pentanoic acid)
29	$CH_3(CH_2)_4COOH$	Caproic Acid (n–Hexanoic acid)
30		Citric Acid (In lemon)
31	$CH_2=CH-COOH$	Acrylic Acid
32	$HO-C(=O)-OH\ (H_2CO_3)$	Carbonic Acid
33	$CH_3-CO-COOH$	Pyruvic Acid
34	$CH_3-CH=CH-COOH$	Crotonic Acid
35	$C_6H_5-CH(OH)-COOH$	Mendalic Acid
36	NH_2COOH	Carbamic Acid (Amino formic Acid)

S.No.	Compound	Common Name
37	$(COOH)_2$	Oxalic acid

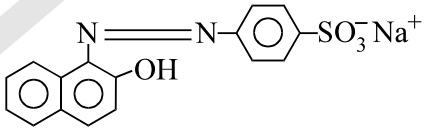
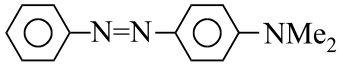
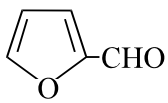
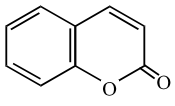
Group J:→ACID DERIVATIVES

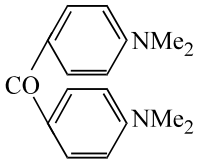
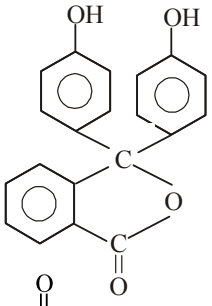
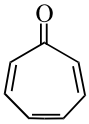
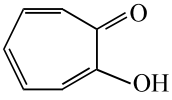
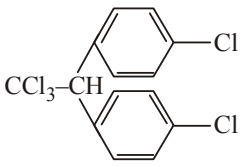
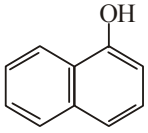
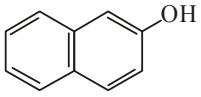
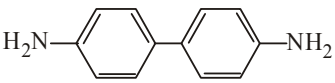
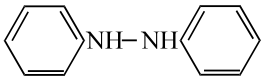
38	$Cl-C(=O)-C(=O)-Cl$	Oxalyl Chloride
39	NH_2COONH_4	Ammonium Carbamate
40	$NH_2-C(=O)-C(=O)-NH_2$	Oxanamide
41	$Cl-C(=O)-Cl$	Phosgene

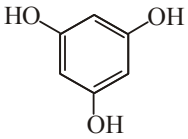
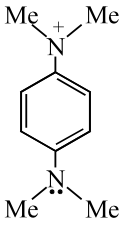
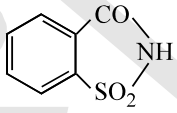
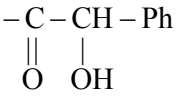
Group K:→N–DERIVATIVES

42	$H-C\equiv N$	Formo Nitrile
43	$CH_3-C\equiv N$	Aceto Nitrile
44	$CH_3-N=C=O$	MIC (Methylisocyanate)

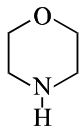
Group L:→AROMATIC COMPOUNDS

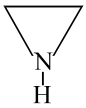
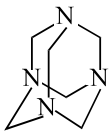
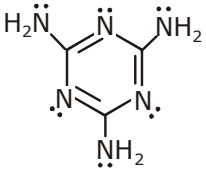
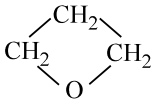
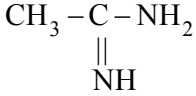
45		Orange II
46		Butter Yellow
47		Furfural
48		Coumarine

S.No.	Compound	Common Name
49		Michler's Ketone
50		Phenolphthalein
51		Tropone (Cycloheptatrienone)
52		Tropolone (Cycloheptatrienolone)
53		DDT (Dichlorodiphenyltrichloroethane)
54		α–naphthol
55		β–naphthol
56		Benzidine
57		Hydrazobenzene

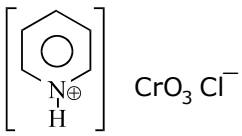
S.No.	Compound	Common Name
58		Phloroglucinol
59		Wurster salts
60	$C_6H_5CONH_2$	Benzamide
61	$(C_6H_5CO)_2O$	Benzoic Anhydride
62	$(C_6H_5CO)_2O_2$	Benzoyl Peroxide
63		Saccharin (o-sulphobenzoic imide)
64	$C_6H_5CH=CH_2$	Styrene
65	Ph–CH=CH–Ph	Stilbene
66		Benzoin
67	$C_6H_5COCOC_6H_5$	Benzil
68	$(C_6H_5)_2C(OH)CO_2H$	Benzilic acid

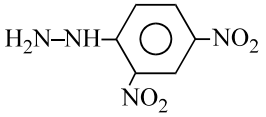
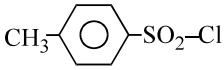
Group M:→ HETROCYCLIC COMPOUNDS

69		Morpholine

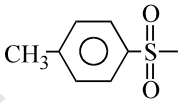
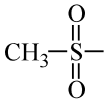
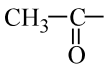
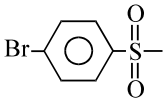
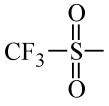
S.No.	Compound	Common Name
70		Aziridine
71		Hexa-methylenetetramine or Urotropine
72.		Malamine
73		Oxitane
74		Amidine

SOME REAGENTS

75	LAH	Lithium aluminium hydride : $LiAlH_4$
76	SBH	Sodium borohydride $NaBH_4$
77	PCC	Pyridinium chlorochromate 
78	Wilkinson's catalyst $(PPh_3)_3Rh^{\oplus}Cl^{-}$	Tris(Triphenylphosphine) chlororhodium (I)
79	Bayer's reagent	1% dil. alkaline aq.sol. of $KMnO_4$

S.No.	Compound	Common Name
80	Braddy's reagent 2,4 DNP	
81	Liemieux reagent	$NaIO_4$ + dil.alk.$KMnO_4$
82	TEL	Tetra ethyl lead
83	Gillman's reagent	$R_2CuLi/[R_2Cu]^{-}Li^{+}$
84	Tollen's reagent	alk. sol. of $AgNO_3$
85	Fehling's reagent	alk. sol. of $CuSO_4$
86	Hinsberg's reagent	

SOME GROUPS

87	Ts	Tosyl	
88	Ms	Mesyl	
89	Ac	Acyl	
90	Bs	Brosyl	
91	Tf	Triflate	

HYDROCARBON GROUPS

If one hydrogen (or more hydrogen atoms in some cases) is taken out from a hydrocarbon, the group left is known as a hydrocarbon group. Hydrocarbons are of three major types, hydrocarbon groups too belong to three main class; these are ;

(1) Acyclic hydrocarbon groups (2) Alicyclic hydrocarbon groups

(3) Aromatic benzenoid hydrocarbon groups

Acyclic Hydrocarbon Groups

Alicyclic hydrocarbon groups are of three types :

(i) Alkyl groups (ii) Alkenyl groups (iii) Alkynyl groups

(i) Alkyl groups : These are univalent groups or radicals obtained by the removal of one hydrogen atom from a molecule of an alkane. The symbol '**R**' is often used to represent an alkyl group. The general formula of an alkyl group is C_nH_{2n+1}.

$$R - H \xrightarrow{-H} R -$$

$$C_nH_{2n+2} \xrightarrow{-H} C_nH_{2n+1}-$$

Alkyl groups are of five types :

(a) Normal Alkyl group : This is formed by the removal of one primary hydrogen atom from the straight chain alkane. A normal alkyl group is written as *n*-alkyl group is common naming system and in its IUPAC namenclature, the prefix n – is dropped.

Some examples are :

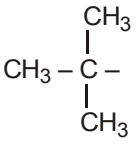
R	Common name	IUPAC name
$CH_3 - CH_2 - CH_2 -$	*n* - Propyl (*n* – Pr)	Propyl (Pr)
$CH_3 - CH_2 - CH_2 - CH_2 -$	*n* - Butyl (*n* - Bu)	Butyl (Bu)
$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 -$	*n* - Pentyl	Pentyl

(b) Secondary alkyl group : This is formed by the removal of one hydrogen from the secondary carbon atom from alkane. It is denoted by *sec* – alkyl or *S* - alkyl group in both of the system of nomenclature.

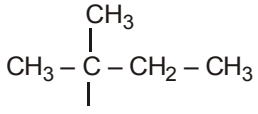
Some examples are given below :

Structure	Common name	IUPAC name
$CH_3 - CH_2 - \underset{\vert}{CH} - CH_3$	*Sec* - butyl (S-Bu)	1-methyl propyl

(c) Tertiary alkyl group : This group is formed by the removal of one hydrogen from the tertiary carbon of the corresponding alkane. It is denoted by *tert* or *t*-alkyl group in both system of nomenclature. Some example are :

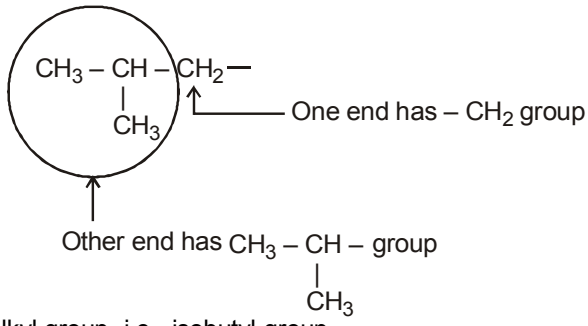


Tert butyl (t-Bu)



tert - pentyl

(d) Isoalkyl group : An alkyl group containing one terminal CH_2 – group and $CH_3-CH(CH_3)-$ group on the other end with no other branching is said to be an *isoalkyl* group or *i*-alkyl group.



Hence, it is isoalkyl group, i.e., isobutyl group.

$CH_3-CH_2-CH(CH_3)-CH_3$ It is not *isobutyl* group

monovalent carbon is not CH_2 –

$CH_3-CH(CH_3)-CH_2-CH_2-$ Isopentyl (or Isoamyl group)

$CH_3-CH(CH_3)-CH_2-CH_2-CH_2-$ Isohexyl group

(e) Neoalkyl group : A neoalkyl group contains one CH_2 – group on one end and one $CH_3-C(CH_3)_2-$ group on the other end with no other branching in the chain.

$CH_3-C(CH_3)_2-CH_2-$ Neopentyl group

$CH_3-C(CH_3)_2-CH_2-CH_2-$ Neohexyl group

$CH_3-C(CH_3)_2-CH_2-CH_2-CH_2-$ Neoheptyl group

Note : Methylene group : If two hydrogen atoms are removed from methane then the group obtained is methylene group, i.e., $-CH_2-$

Alkenyl group

Hydrocarbon group containing carbon-carbon double bond is called alkenyl group. Their common names are accepted in IUPAC system in most of the cases. Some examples are :

$CH_2=CH-$	Vinyl group
$CH_2=CH-CH_2-$	Allyl group
$CH_3-CH=CH-$	Propenyl group
$CH_3-CH=$	Ethylidene
$CH_3-CH_2-CH=$	Propylidene
$CH_3-C(CH_3)=$	1-methyl ethylidene

Alkynyl group

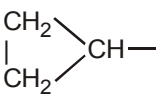
Hydrocarbon group containing carbon-carbon triple bond may be called an alkynyl group. Their common names are accepted in IUPAC system in most of the case. Some examples are :

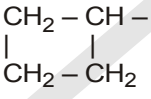
Structure	Common name	IUPAC name
$C\equiv$	Methynyl	Methynyl
$CH\equiv C-$	Ethynyl	Ethynyl
$CH\equiv C-CH_2-$	Propargyl	Propargyl
$CH_3-C\equiv C-$	Propynyl	Propynyl

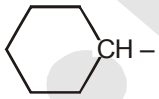
Alicyclic Hydrocarbon Groups

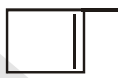
These are obtained when one hydrogen atom is removed from the ring carbon. These groups may be classified as :

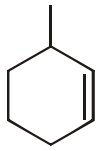
cycloalkyl groups


Cyclopropyl


Cyclobutyl

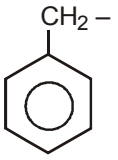

Cyclohexyl

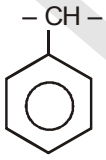

1-Cyclobutenyl

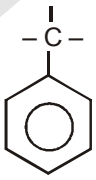

2-Cyclohexenyl

Aromatic Benzenoid Hydrocarbon Groups

Aromatic hydrocarbon groups have one or more hydrogen atoms less than the present hydrocarbons. These are in general denoted by Ar- and called aryl groups. The simplest aryl group is phenyl group (C_6H_5). This is denoted by Ph or ϕ.


Benzyl


benzal


benzo

Class of Compound	Structure	Common name
Alkanes	(i) CH_4	Methane
	(ii) $CH_3 - CH_3$	Ethane
	(iii) $CH_3 - CH_2 - CH_3$	Propane
	(iv) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{\vert}{\overset{\vert}{CH}}}}-CH_3$	Isobutane
	$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{\vert}{\overset{\vert}{C}}}}-CH_3$	Neopentane
Alkenes	$CH_2 = CH_2$	Ethylene
	$CH_3 - CH = CH_2$	Propylene
Alkynes	$CH \equiv CH$	Acetylene
	$CH_3 - C \equiv CH$	Methyl acetylene
	$CH_3 - C \equiv C - CH_3$	Dimethyl acetylene
Alkyl halides	$CH_3 - X$	Methyl halide
	$CH_3-\underset{\displaystyle Br}{\overset{\displaystyle CH_3}{\underset{\vert}{\overset{\vert}{CH}}}}-CH_3$	Isopropyl bromide
	$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle Br}{\underset{\vert}{\overset{\vert}{C}}}}-CH_3$	Tert-butyl bromide
	$CH_3-\underset{\displaystyle Br}{\overset{\displaystyle CH_3}{\underset{\vert}{\overset{\vert}{CH}}}}-CH_2-CH_3$	Sec-butyl bromide
	$CH_3 - CHCl_2$	Ethylidene dichloride
	$CH_2Cl - CH_2Cl$	Ethylene dichloride
Alcohol	$CH_3 - OH$	Methyl alcohol
	$CH_3 - CH_2 - OH$	Ethyl alcohol
	$CH_3 - CH_2 - CH_2 - OH$	*n* - Propyl alcohol
	$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2OH}{\underset{\vert}{\overset{\vert}{CH}}}}$	Isobutyl alcohol
	$HO - CH_2 - CH_2OH$	Glycol
	$OHCH_2 - CHOH - CH_2OH$	Glycerol
Ether	$CH_3 - O - CH_3$	Dimethyl ether
	$CH_3 - CH_2 - O - CH_3$	Ethyl methyl ether
	$CH_3 - CH_2 - O - CH_2 - CH_3$	Diethyl ether

Class of Compound	Structure	Common name
	$CH_3 - CH_2 - CH_2 - O - \underset{\displaystyle CH_3}{\underset{\vert}{CH}} - CH_3$	Isopropyl propyl ether
Aldehydes	$HCHO$	Formaldehyde
	$CH_3 - CHO$	Acetaldehyde
	$CH_3 - CH_2 - CH_2 - CHO$	Butyraldehyde
Ketones	$CH_3 - \overset{\displaystyle O}{\overset{\Vert}{C}} - CH_3$	Acetone
	$CH_3 - CH_2 - \overset{\displaystyle O}{\overset{\Vert}{C}} - CH_3$	Methyl ethyl ketone
	$CH_3 - CH_2 - \overset{\displaystyle O}{\overset{\Vert}{C}} - CH_2 - CH_2 - CH_3$	Ethyl propyl ketone
Carboxylic acids	$HCOOH$	Formic acid
	$CH_3 - COOH$	Acetic acid
	$CH_3 - CH_2 - CH_2 - COOH$	Butyric acid
	$\begin{matrix} COOH \\ \vert \\ COOH \end{matrix}$	Oxalic acid
	$CH_2 \begin{matrix} \diagup COOH \\ \diagdown COOH \end{matrix}$	Malonic acid
	$\begin{matrix} CH_2 - COOH \\ \vert \\ CH_2 - COOH \end{matrix}$	Succinic acid
	$CH_2 \begin{matrix} \diagup CH_2 - COOH \\ \diagdown CH_2 - COOH \end{matrix}$	Glutaric acid
Esters	$HCOOCH_3$	Methyl formate
	$CH_3COOC_2H_5$	Ethyl acetate
	$CH_3 - CH_2 - CH_2 - COOC_2H_5$	Ethyl butyrate
Anhydrides	$CH_3 - \overset{\displaystyle O}{\overset{\Vert}{C}} - O - \overset{\displaystyle O}{\overset{\Vert}{C}} - CH_3$	Acetic anhydride
	$CH_3 - CH_2 - \overset{\displaystyle O}{\overset{\Vert}{C}} - O - \overset{\displaystyle O}{\overset{\Vert}{C}} - CH_2 - CH_3$	Propionic anhydride
Acid chlorides	$CH_3 - \overset{\displaystyle O}{\overset{\Vert}{C}} - Cl$	Acetyl chloride
Cyanides	$CH_3 - CN$	Methyl cyanide
	$CH_3 - CH_2 - CN$	Ethyl cyanide

Any given organic structure has only one IUPAC name and any given IUPAC name represents only one molecular structure.

The IUPAC name of any organic compound essentially consists of three parts, i.e.,

(1) root word (2) Suffix and (3) Prefix

ROOT WORD

If is the basic unit of the name. If denotes the number of carbon atoms present in the principal chain of the molecule. Chain containing one to four carbon atoms are known by special root words (based upon the common names of alkanes) while chains from C_5 onwards are known by Greek number roots. Thus :

Chain length	Word root	Chain lengh	Word root	Chain length	Word root
C_1	Meth	C_8	Oct	C_{14}	Tetradec
C_2	Eth	C_9	Non	C_{20}	Eicos
C_3	Prop	C_{10}	Dec	C_{30}	triacont
C_5	Pent	C_{11}	Undec	C_{40}	Tetracont
C_6	Hex	C_{12}	Dodec	C_{50}	Pentacont
C_7	Hept	C_{13}	Tridec	C_{60}	Hexacont

SUFFIX

There are two types of suffixes, i.e., Primary suffix and Secondary suffix.

(a) Primary suffix : A primary suffix is always added to the root word to indicate whether carbon chain is saturated or unsaturated. The primary suffix for the various saturated and unsaturated carbon chains and groups are given below :

Nature of carbon chain	Primary surfix	Chain lengh
Saturated, C – C	–ane	Alkane
Unsaturated, C = C	–ene	Alkene
Unsaturated, C ≡ C	–yne	Alkyne

Nature of group	Primary suffix	Generic name
Alkane – one hydrogen atom	–yl	Alkyl
Alkene – one hydrogen atom	–enyl	Alkenyl
Alkyne – one hydrogen atom	–ynl	Alkynyl

If the parent, carbon-chain contains two, three, four or more double or triple bonds, numerical prefixes such a di (for two), tri (for three), tetra (for four) etc. are added to the primary suffix. For example :

	Type of carbon chain	*Primary suffix*	*Generic name*
(i)	Having two double bonds	diene	Alkadiene
(ii)	Having three double bonds	triene	Alkatriene
(iii)	Having n double bonds	polyene	Alkapolyene
(iv)	Having two triple bonds	diyne	Alkadiyne
(v)	Having three triple bonds	triyne	Alkatriyne

(b) **Secondary suffix :** Suffix added after the primary suffix to indicate the particular functional group (groups) present in the carbon chain is known as secondary suffix. Secondary suffix of some important functional groups are given below.

Class of organic compounds	*Functional group*	*Secondary suffix*	*Class of organic compounds*	*Functional group*	*Secondary suffix*
Alcohols	– OH	–ol	Acid chlorides	– COCl	–oyl chloride
Aldehydes	– CHO	–al	Esters	– COOR	Alkyl... oate
Ketones	– CO –	–one	Nitrilie	– CN	nitrile
Carboxylic acids	– COOH	–oic acid	Amide	– $CONH_2$	–amide

It may be noted that while adding the secondary suffix to the primary suffix, the terminal 'e' of the primary suffix (i.e., ane, ene, yne) is dropped if the secondary suffix begins with **a, e, i, o, u, & y** but is retained if the secondary suffix begins with a **consonant except *y*.**

Structure	root Word	Primary suffix	Secondary suffix	IUPAC name
$CH_3 - CH_2 - OH$	Eth	ane	ol	Ethanol
$CH_3 - CH_2 - CH_2 - CHO$	But	ane	al	Butanal
$CH_2 = CH - \overset{\overset{O}{\|\|}}{C} - CH_3$	But	ene	one	Butenone
$CH_3 - (CH_2)_4 - COOH$	Hex	ane	oic	Hexanoic acid

Prefix

Prefixes are used to indicate

(i) the cyclic nature of compound and

(ii) the nature of the substituents present on the parent chain. Thus, prefixes are of two types :

(a) Primary prefix : The primary prefix cyclo is added before the root word of indicate the cyclic nature of the compound.

Thus

$$\begin{matrix} CH_2 - CH_2 \\ | \quad\quad | \\ CH_2 - CH_2 \end{matrix}$$ Cyclo + but + ane

Primary prefix word-root Primary suffix

$\Downarrow$

Cyclobutane

In open chain compound no prefix (primary) is added.

(b) Secondary prefix : In IUPAC system of nomenclature, certain functional groups are not considered as functional groups but instead are treated as substituents. These are called secondary prefix and are added immediately before the root word (or the primary prefix in case of alicyclic compounds) in **alphabetical** order to denote the side chains or substituent groups. The secondary prefixes for some groups which are always treated as substituent groups are given below :

Substituent group	Secondary prefix	Substituent group	Secondary prefix
–F	Fluoro	– OR	Alkoxy
– Cl	Chloro	$-\overset{\oplus}{N}\equiv N$	Diazo
–Br	Bromo	$-NH_2$	Amino
–I	Iodo	$-CH_3$	Methyl
$-NO_2$	Nitro	$-C_2H_5$	Ethyl
– NO	Nitroso	$CH_3-CH_2-CH_2-$	Propyl
$CH_3-\underset{\vert}{CH}-CH_3$	1-methyl ethyl	$CH_3-\underset{\vert}{\overset{CH_3}{\overset{\vert}{C}}}-CH_3$	1-1-dimethyl Ethyl

The order of IUPAC naming given below

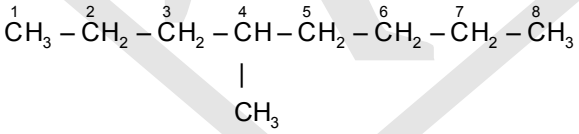
Secondary prefix + Primary prefix + word root + primary suffix + secondary suffix.

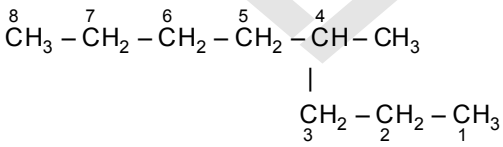
Secondary prefix – primary prefix - generic name

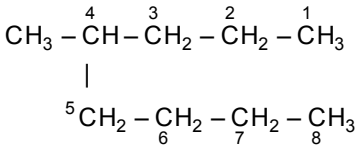
IUPAC Nomenclature of Branched-chain Alkanes

Branched-chain alkanes are named according to the following rules :

1. **Longest Chain Rule :** Locate the longest continuous chain of carbon atoms. This chain determines the parent name of the alkane. Notic that the longest continuous chain is chosen regardless of how the molecule is written.

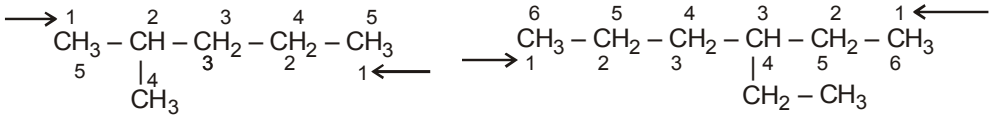






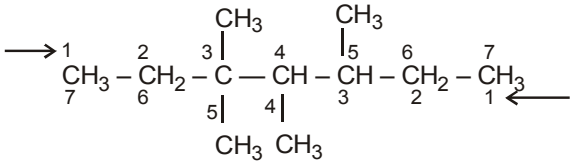
(2) **Lowest Locant Rule or Lowest Sum Rule :** The carbon atoms of the longest continuous chain, i.e., parent chain are numbered by arabic numerals 1, 2, 3, 4 ..... from one end of the chain to the other. in such a manner that carbon atom carrying first substituent gets the lowest number. The number that locates the position of the substituent is known as **locant.**

However, if there are two or more substituents, the numbering of parent chain is done in such a way that the sum of locants is the lowest. This is called the **lowest sum rule.**



2-Methylpentane
not
4-Methylpentane

3-Ethylhexane
not
4-Ethylhexane



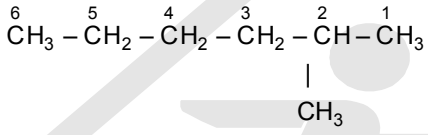
3,3, 4, 5-Tetramethylheptane

Position of the substituents should be 3, 3, 4 and 5 because

Position should not be 3, 4, 5 and 5 because

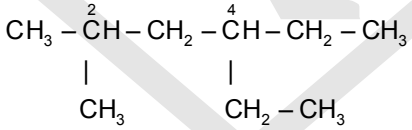
$3 + 4 + 5 + 5 = 17$

3. **Name of the Branched chain Alkane :** The substituent name and the parent alkane are joined in one word and there is a hyphen between the number and the substituent name.



2 – Methylhexane not 2 – Methyl hexane

4. **Alphabetical order of the side chains :** When two or more substituents are present, give each substituent a number corresponding to its position on the longest chain. The substituent groups be listed alphabetically.

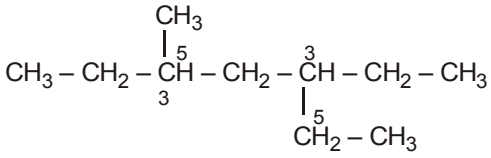


4 – Ethyl – 2 – methylhexane

not

2 – Methyl – 4 – ethylhexane

5. **Numbering of different alkyl groups at equivalent positions :** If two different alkyl groups are present at equivalent positions the numbering of the parent chain is done in such a way that alkyl group which comes first in the alphabetical order gets the lower number. For example :

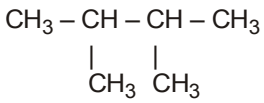


3-Ethyl-5-methylheptane
not
5-Ethyl-3-methylheptane

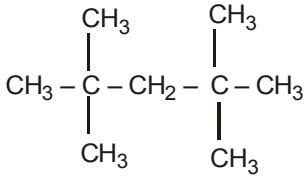
Note **:** In some books it is mentioned that if different alkyl groups are present as substituents on the identical positions then numbering must be done so as to give the smallest alkyl group the minimum number but it is not the case.

(6) **Naming of Some Alkyl groups at different positions :** When two or more substituents are identical, indicate this by the use of prefixes *di, tri, tetra* and so on. Then make certain that each and every substituent has a number. Commas are used to separate numbers from each other.

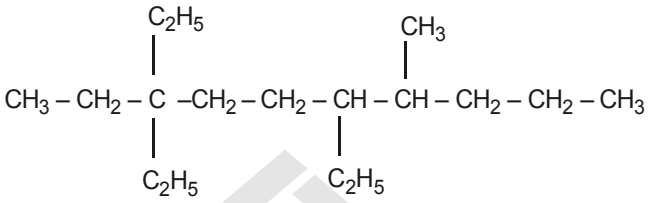
Note **:** The prefixes *di, tri, tetra, sec*, *teri* are ignored in alphabetising substituent groups. The prefixes *iso, neo* and *cyclo* are not igonored, For example :



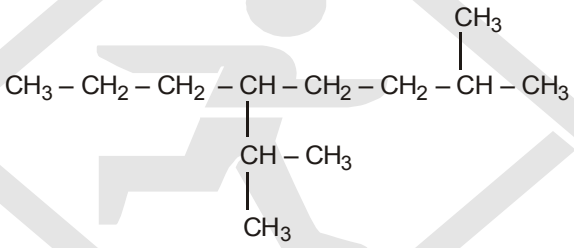
2,3-Dimethylbutane



2,2,4,4-Tetramethylpentane

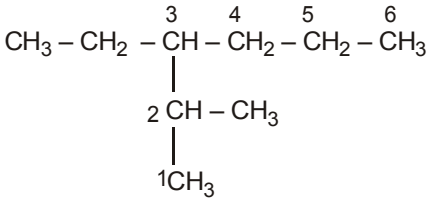


3,3,6-Triethyl-7-methyldecane not 7-Methyl-3, 3,6-triethyldecane

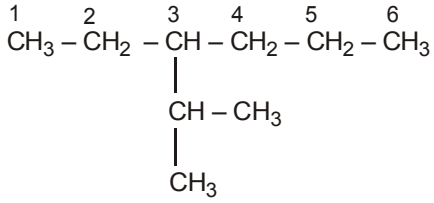


5-Isopropyl-2-methyloctane not 2-Methyl-5-isopropylocatane

(7) **Rule for larger number of Substituents :** If a compound has two or more chains of the same length, the parent hydrocarbon is the chain with the greater number of substituents.



3-Ethyl-2-methylhexane
(two substituents) $\Rightarrow$ correct name

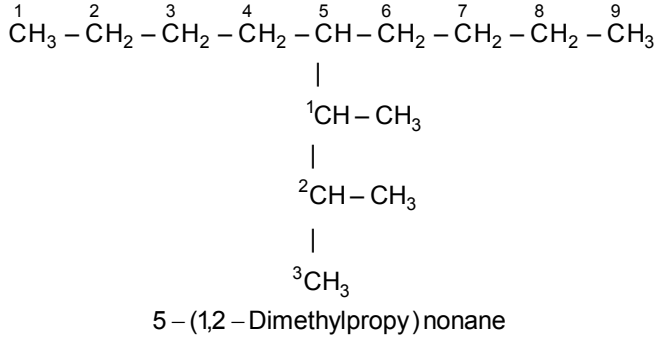


3-Isopropylhexane
(one substituents) $\Rightarrow$ wrong name

(8) **Numbering the Complex Substituent :** Name such is isopropyl, *sec* butyl and *tert* butyl are acceptable substituent names in the IUPAC system of nomenclature but systematic substituent name are preferable.

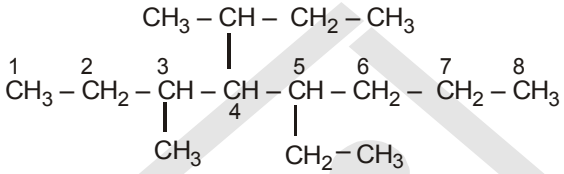
Systematic substituent name are obtained by numbering the substituent starting at the carbon that is attached to the parent hydrocarbon. This means that the carbon that is attached to the parent

hydrocarbon is always the number-1 carbon of the substituent. In a compound such as 5-(1,2-dimethylpropyl) nonane, the complex substituent is in parentheses; the numbers inside the parentheses indicate the position on the substituent, whereas the number outside the parentheses indicates a position on the parent hydrocarbon.



5 – (1,2 – Dimethylpropy) nonane

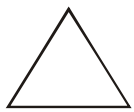
Problem 1. Give IUPAC name of the compound



Sol. :

NOMENCLATURE OF CYCLOALKANES

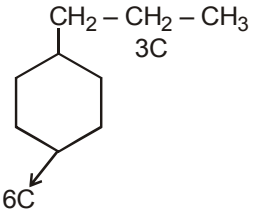
(1) Cycloalkanes are named by adding primary prefix before parent name (i.e., alkane). For example :



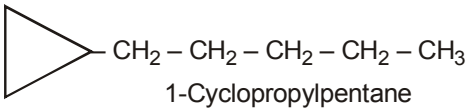
Cyclopropane

Cyclohexane

(2) In the case of alkyl substituted cycloalkanes, the ring is the parent hydrocarbon unless the substituent has more carbon than the ring. In that case, the substituent is the parent hydrocarbon and the ring is named as a substituent.

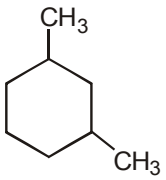


Propylcyclohexane

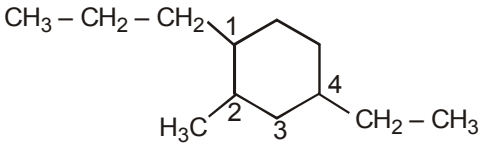


1-Cyclopropylpentane

(3) If there is more than one substituent on the ring, the substituents are represented in alphabetical order. One of the substituents is given the number I position and the ring is numbered from that position in a direction (either clockwise or anticlockwise) that gives a second substituents the lowest possible number.



1,3-Dimethylcyclohexane

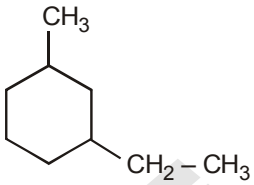


4-Ethyl-2-methyl-1-propylcyclohexane
not
1-Ethyl-3-methyl-4-proplcyclohexane

because 4 + 2 + 1 = 7

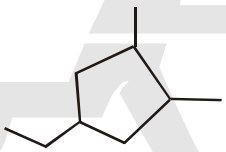
1 + 3 + 4 = 8

(4) If the ring has only two substituents and they are different, the substituents are cited in alphabetical order and the number 1 position is given to the first cited substituent.



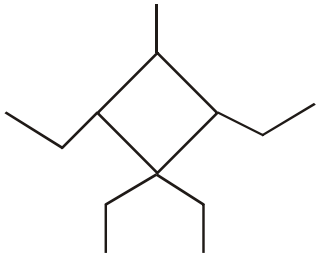
1-Ethyl-3-methylcyclohexane
not
3-Ethyl-1-methylcyclohexane

Problem 2. Name the following compound :



Sol.

Problem 3 : ***The IUPAC name of the compound***

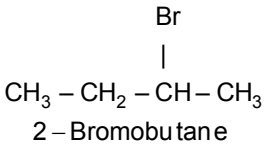


Sol.

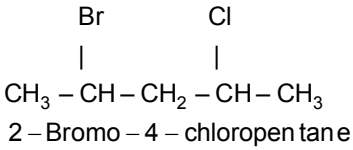
NOMENCLATURE OF SUBSTITUTED ALKANES (HAVING TWO FUNCTIONAL GROUPS) OR NOMENCLATURE OF ALKANES HAVING SECONDARY PREFIX

Alkyl Halides

(i) They are named as substitued alkanes, i.e., Haloalkanes. Some examples are :



2 – Bromobutane

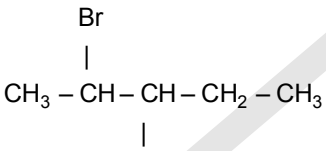


2 – Bromo – 4 – chloropentane

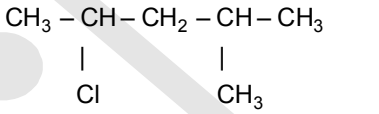
not

2 – Chloro – 4 – bromopentane

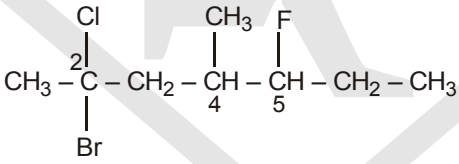
(ii) When the parent chain has both a halo and an alkyl group, number the chain from the end nearer the first substituent, regardless of whether it is halo or alkyl group. If two substituents has equal number from the end of the chain, then number the chain from the end nearer the substituent that has alphabetical precedence.



2 – Bromo – 3 – methylpentane



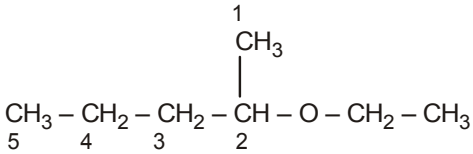
2 – Chloro – 4 – methylpentane



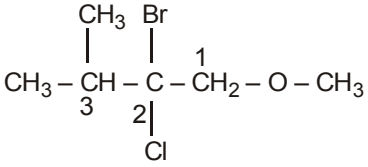
2-Bromo-2-chloro-5-fluoro-4-methylheptane

Nomenclature of Ethers

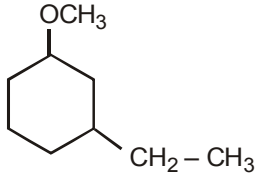
In the IUPAC system ethers are named as alkoxy alkanes. The large alkyl group is chosen as the parent alkane.



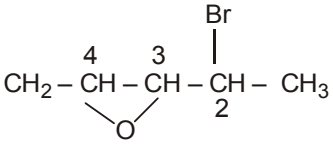
2-Ethoxypentane



2-Bromo-2-chloro-1-methoxy-3-methylbutane



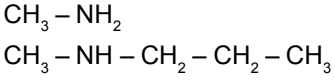
3-ethyl 1-Methoxycyclohexane



2-Bromo-3,4-epoxypentane

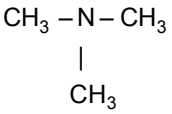
NOMENCLATURE OF AMINES

(a) Common Name : The common name of amine is obtained by citing the name of the alkyl groups bonded to the nitrogen atom in alphabetical order followed by **amine.** The entire name is written in one word. For examples.

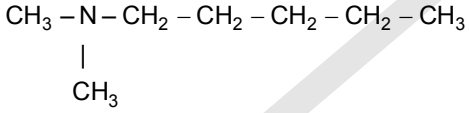


Methylamine

Methylproplyamine



Trimethylamine



Dimethylpentylamine

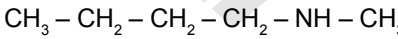
(b) IUPAC Name :

(i) The generic name of amines is alkanamine. The 'e' at the end of the alkane name for the longest continuous carbon chain in the amine is replaced by amine.

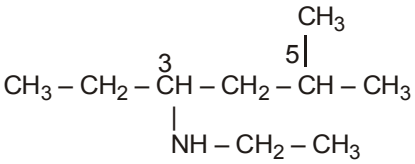
(ii) Position of nitrogen is denoted by least possible number in the longest possible carbon chain.

(iii) The name of any other alkyl groups bonded to nitrogen (in secondary and tertiary amines) is preceided by an N to indicate that group is bonded to a nitrogen rather than to a carbon.

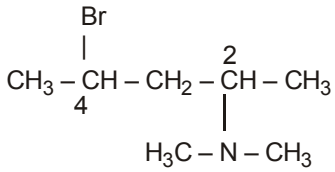
(iv) All substituents, whether they are attached to nitrogen or to the parent chain or listed in alphabetical order.



N-methyl-1-butanamine or N-methyl butan-1-amine



N-Ethyl-5-methyl-3-hexanamine



4-Bromo-N, N-dimethyl-2-pentanamine

NOMENCLATURE OF ALKENES

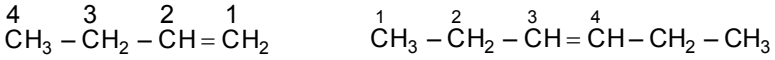
The following rules are used for naming alkene :

(1) Determine the parent name by selecting the longest chain that contains the double bond. General parent names are :

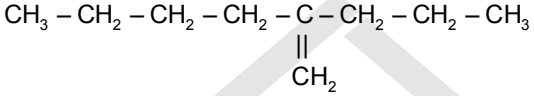
Alkene	:	One double bond
Alkadiene	:	Two double bonds
Alkatriene	:	Three double bonds
Alkatetraene	:	Four double bonds

(2) The longest continuous chain containing the functional group **double bond** is numbered in a direction that gives the functional group the lowest possible number.

Designate the position of double bond by using the number of the first carbon atom of the double bond. For example, 1- butene signifies that double bond is between first and second carbon; 3-hexene signifies that double bond is present between carbon-3 and carbon-4

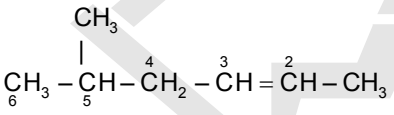


(3) The parent chain must contain the functional group (multiple bond) regardless of the fact whether it also denotes the longest continuous chain of carbon or not. For example :

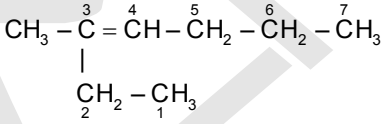


The longest continuous chain has eight carbons but the longest continuous chain containing double bond has six carbons, so the parent name of the compound is hexene.

(4) If the chain has the substituents, it is still numbered in the duration that gives the functional group the lowest possible number. For example :

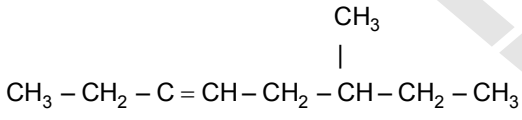


5 – Methyl – 2 – hexene

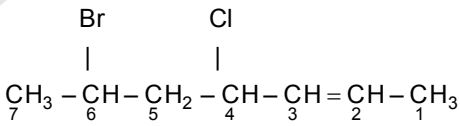


3 – Methyl – 3 – heptene

(5) If a chain has more than one substituent the substituents are cited in alphabetical order as in case of alkenes.

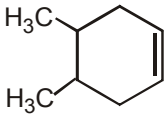


3,6 – Dimethyl – 3 – octene



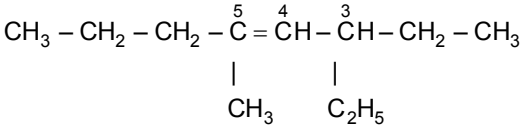
6 – Bromo – 4 – chloro – 2 – heptene

(6) In cycloalkenes, a number is not needed to denote the position of the functional group since the ring is always numbered so that the double bond is between carbon-1 and carbon-2.

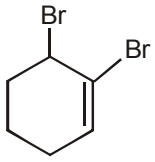


4,5-Dimethylcylohexene

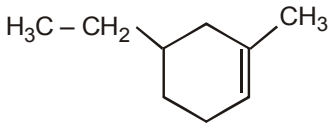
(7) If the same number for the double bond is obtained in both directions, the correct name is the one that contains the lowest substituent number. (not sum of the lowest substituents)



3 – Ethyl – 5 – methyl – 4 – octene not 6 – Ethyl – 4 – methyl – 4 – octene

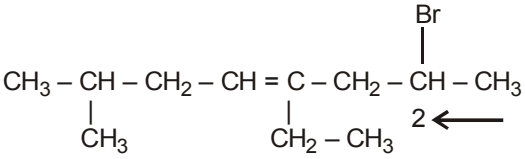


1,6-Dibromocyclohexene



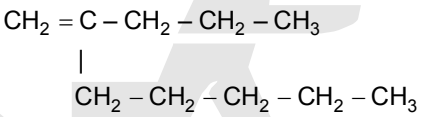
5-Ethyl-1-methylcyclohexane

(8) If both directions lead to the same number for the functional group (double bond) and the same low numbers for one or more substituents, then these substituents are ignored and the direction is chosen that given the lowest number to one of the remaining substituents.



2-Bromo-4-ethyl-7-methyl-4-octene
not
7-Bromo-5-ethyl-2-methyl-4-octene
because 4 < 5

Problem 4 : Name of given compound using IUPAC nomenclature



Sol.

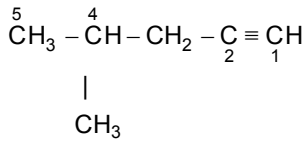
NOMENCLATURE OF ALKYNES

(i) Alkynes are named in the same way as the alkanes.

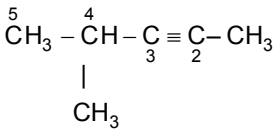
(ii) The general parent names are :

Alkyne	:	One triple bond
Alkadiyne	:	Two triple bonds
Alkatriyne	:	Three triple bonds
Alkatetrayne	:	Four triple bonds

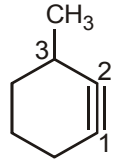
The IUPAC names of some alkynes are given below :



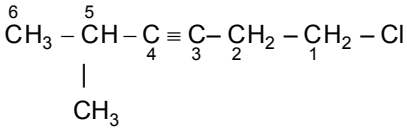
4 – Methyl – 1 – pentyne



4 – Methyl – 2 – pentyne



3-Methy cyclo hex-1-yne

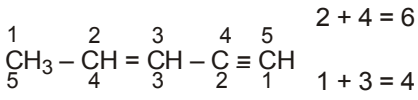


1 – Chloro – 5 – methyl – 3 – hexyne

NOMENCLATURE OF HYDROCARBONS HAVING DOUBLE AS WELL AS TRIPLE BONDS

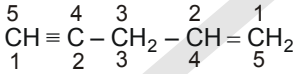
(1) When double and triple bonds are present, the hydrocarbon is named as **alkenyne.** ≡ **alk + en + yne**

(2) The numbering of the parent should always be done from that end which has lowest sum for the multiple bonds. For example.

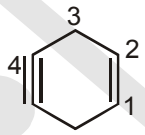


Pent-3-en-1-yne

(3) If, however, there is a choice in numbering, the double bond is always given preference over the triple bond.

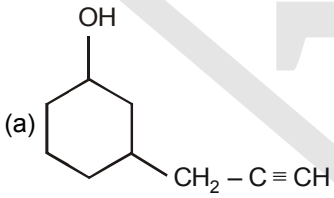


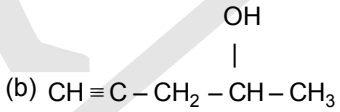
Pent-1-en-4-yne



Cyclohex-1-en-4-yne

Promblem 5. Name the given compound using IUPAC nomenclature





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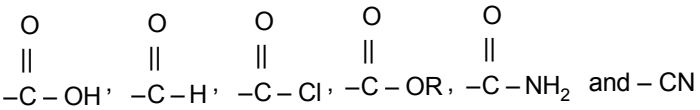
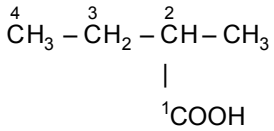
(3) When a chain compound has terminating functional group

Chain terminating functional groups are those groups in which carbon of the functional group is monovalent. Examples are



When a chain terminating functional group is present, it is always given number - 1 and number one is usually omitted from the final name of the compound.



(4) When compound contains two or more like groups, the numerical prefixes di, tri etc. are used and the terminal 'e' from the primary suffix is retained while writing the IUPAC name.

For example : $CH_3 - CHOH - CHOH - CH_3$

2,3-Butanediol

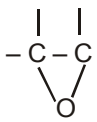
NOMENCLATURE OF POLYFUNCTIONAL COMPOUNDS

(1) **Principal functional group :** When an organic compound contains two or more different functional group, one of the functional group is selected as the principal funtional group while all other groups (secondary functional group) are treated as substituents.

The choice of principal functional group is made on the basic of the following order of preference.

$$-SO_3H > -COOH > -\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}- > -\overset{O}{\overset{\|}{C}}-OR > -\overset{O}{\overset{\|}{C}}-Cl > -CONH_2 > -CN > -CHO > -CO > -OH$$

Prefix name of different functional groups are as follows :

Group	Secondary prefix Name	Secondary Surfix
– COOH	Carboxy	Oic acid
$-SO_3H$	Sulpho	Sulphonic acid
–COOR	Alkoxy carbonyl	Alkyl oate
– COCl	Chloro formyl	oyl chloride
$-CONH_2$	Carbamoyl	amide
– CN	Cyano	nitrile
– NC	Isocyano	isonitrile
– CHO	Formyl or aldo	al
– CO –	Keto or oxo	one
– OH	Hydroxy	ol
– SH	Mercapto	thiol
$-NH_2$	Amino	Amine
– OR	Alkoxy	
	Epoxy	
– N = N –	Azo	
$-NO_2$	Nitro	
– NO	Nitroso	
– X	Halo	

(2) **Selection of Principal chain :** The principal chain is selected in such a way that it includes the maximum number of functional groups (as substituents) including the principal group.

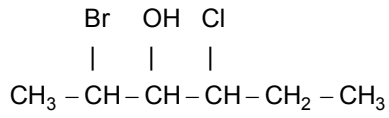
(3) **Numbering of Principal chain :** The principal chain present in polyfunctional compound is numbered in such a way that principal functional group gets the lowest number followed by multiple bonds and the substituents, i.e.,

Principal functional group > double bond > triple bond > substituents

(4) **Alphabetical order :** Substituents, side chains and secondary functional groups are arranged in alphabetical order. To illustrate these rules, let us consider the examples of different class of organic compounds.

IUPAC NAME OF ALCOHOLS

Ex.1



(i) The longest chain has six carbons : hex.

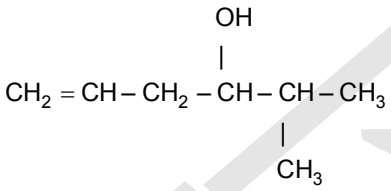
(ii) Compound is saturated. Hexane.

(iii) The alcohol function is designated as ol, hexanol.

(iv) Number the chain to give the – OH the lowest possible number, 3-hexanol.

(v) Name all the substituents with prefixes. The complete name is 2-Bromo-4-chloro-2-hexanol.

Ex.2



(i) The longest chain has six carbons : hex.

(ii) There is presence of double bond, hexene

(iii) The principal functional group is – OH ; hexenol.

(iv) Number the chain to give the – OH group the lowest possible number. Incorporate these numbers in the primary and secondary suffix, 5-Hexen-3-ol. The first number-5-refers the position of double bond and the second number - 3 locates the – OH group.

(v) Name all other substituents with prefixes.

The complete name is 2-Methyl-5-hexen-3-ol. or 2-methyl-hex-5-en-3-ol

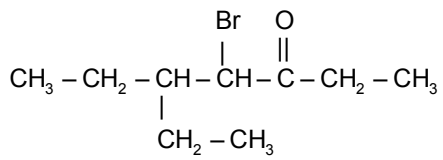
➢ **IUPAC Nomenclature of Aldehydes and ketones**

(A) Ketones : General name of ketones are as follows :

Alkanone	:	one keto group
Alkanedione	:	two keto groups
Alkanetrione	:	three keto groups

Thus 'e' of the hydrocarbon is replaced by **– one** when compound has only one CO group.

Ex.3

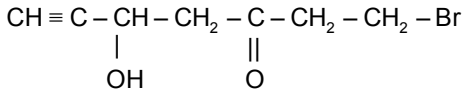


(i) There are seven carbons having keto groups : heptanone.

(ii) Number the chain to give the position of keto group the lowest possible number : 3-heptanone.

(iii) Given name and position of other substituents with respect to keto groups. Thus, the complete name is : 4-Bromo-5-ethyl-3-heptanone

Ex.4



(i) Seven carbon chain : hept

(ii) One carbon-carbon triple bond : heptyne

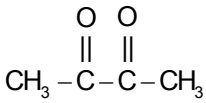
(iii) Principal functional group is keto : heptynone.

(iv) Position of keto should be represented by lowest possible number : 3 - heptynone

(v) Position of other groups and substituents are determined with respect to keto group.

The complete name is : 1 - Bromo - 5 - hydroxy - 6 - heptyn - 3 - one

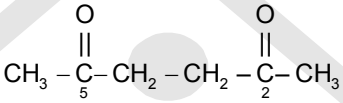
Position of functional group can only be designated if positional isomersim is possible is that given structure.



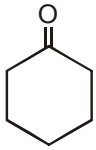
Butanedione

not

2,3 – Butanedione



2,5 – Hexanedione



Cycloalkanone

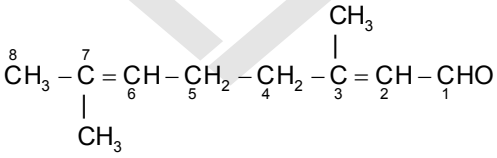
⇓

Cyclohexanone

(B) Aldehydes :

(1) The general name is : Alkanal, Alkenal or Alkynal i.e., 'e' of the hydrocarbon is replaced by **al.**

(2) The position of the aldehydic group does not have to be designated since it is always at the end of the parent hydrocarbon and therefore, is always at the number 1 position.



(i) Compound is derivative of alkadiene having functional group – CHO. Thus, the general name is alkadienal.

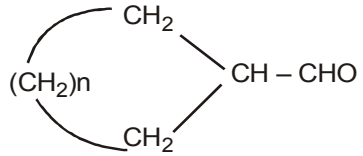
(ii) Principal chain has 8C's hence alkadienal is octandienal.

(iii) Position of – CHO is always 1 and position of other functional groups and substituents are determined with respect to the position of – CHO

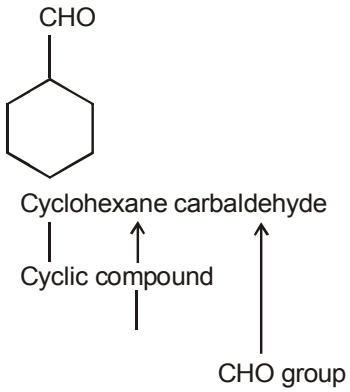
The complete name is 3, 7 – Dimethyl-2,6-octadienal.

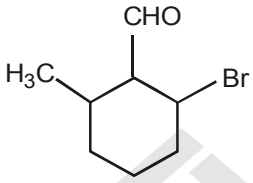
or 3,7-Di methyl octa-2,6-dien-al

Note - 1 : If the aldehyde group is attached to a ring, the aldehyde is named by adding carbaldehyde to the name of the cyclic compound



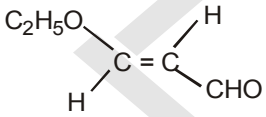
Cycloalkane Carbaldehyde

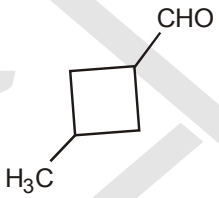


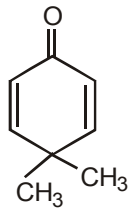


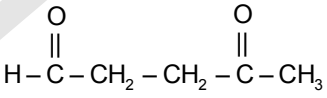
2-Bromo-6-methylcyclohexanecarbaldehyde

Pro.6 Given IUPAC name for the following compound.

(a) 

(b) 

(c) 

(d) 

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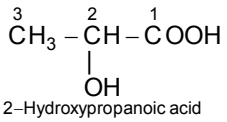
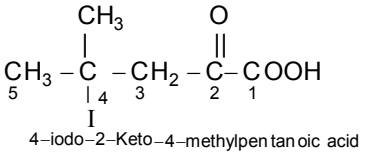
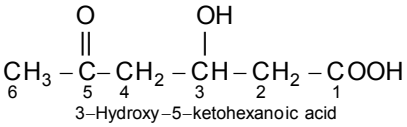
IUPAC Nomenclature of Carboxyclic Acids

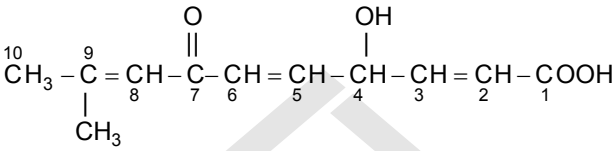
(i) Replace 'e' of the hydrocarbon by **oic acid.**
(ii) For naming a substituted carboxylic acid, the longest possible chain containing carboxylic group is numbered from 1 to n begining with the carboxylic carbon.





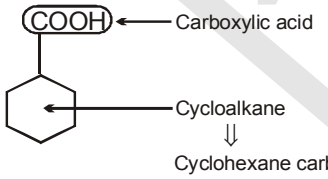


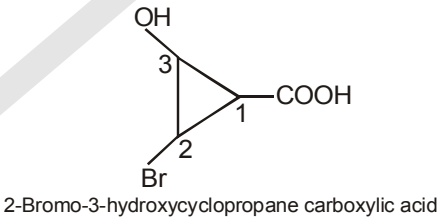
Example :



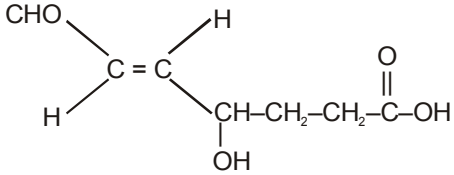
(i) Ten carbon in the longest chain : dec
(ii) Three double bonds : decatriene
(iii) Funcational group is carboxylic : decatrienoic acid
(iv) Three double bound are present at 2, 5 and 8 : 2,5,8-decatrienoic acid.
(v) The other groups are named with prefixes. The complete name is 4-Hydroxy-7-keto-9-methyl-deca-2,5,8-Trien-oic acid.

Note 1 : Carboxylic acid in which carboxylic group is attached to a cyclic compund can be named as Cycloalkanecarboxylic acid or Cycloalkenecarboxylic acid or Cycloalkynecarboxylic acid





Problem 7. ***Provide a IUPAC name for the given compound :***



Sol

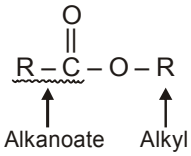
NOMENCLATURE OF ESTERS

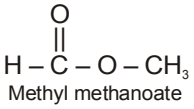
Esters are named in the following way :

(i) The first word of the name is the stem name of the alkyl group attached to oxygen.

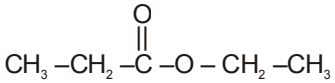
(ii) The second word of the name is the name of the parent acid with the suffix –ic acid replaced by –ate.

(iii) This nomenclature applies for both common and IUPAC name of esters.

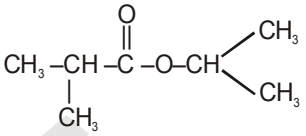




Methyl methanoate



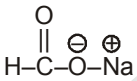
Ethyl propanoate



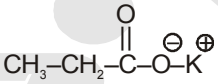
1-methyl ethyl-2-methyl propanoate

Note I : Salts of carboxylic acids are same as follows :

The cation is named first followed by the name of the acid again with ic acid is replaced by ate.

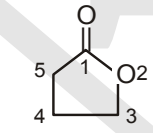


Sodium methanoate

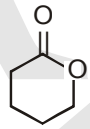


Potassium propanoate

Note 2 : Cylic esters are called lactones. The IUPAC system names these compound as oxacycloalkanone.



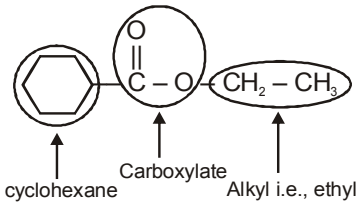
2-Oxacyclopentanone



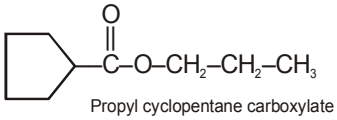
2-Oxacyclohexanone

Note 3 : Esters in which carbonyl group of ester is attached to a cylic system can be named as :

Alkyl cyclo alkane carboxylate



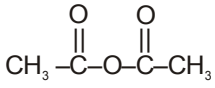
Thus the IUPAC name is ethyl cyclohexane carboxylate



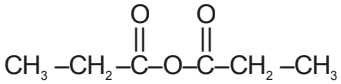
Propyl cyclopentane carboxylate

IUPAC Nomenclature of Anhydrides

(i) Symmetrical anhydrides are named by using the acid name and replacing **acid** with **anhydride**.

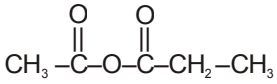


Symmetrical anhydride
Ethanoic anhydride



Propanoic anhydride

(ii) Mixed anhydrides are named by starting the names of both acids in alphabetical order followed by **"anhydride".**



Ethanoic propanoic anhydride

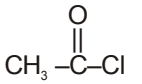
Nomenclature of Acid Chloride

Acid chloride is named by using the acid name and replacing **ic acid** with **yl chloride,** i.e.,

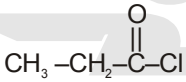
Alkanoic acid $\rightarrow$ Alkanoyl chloride

Alkenoic acid $\rightarrow$ Alkenoyl chloride

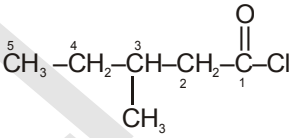
Alkynoic acid $\rightarrow$ Alkynoyl chloride



Ethanoyl chloride



Propanoyl chloride



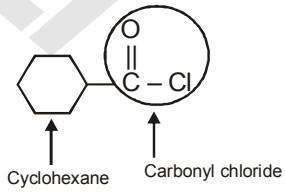
3-Methylpentanoyl chloride

Note : ***Acid chloride in which carbonyl group of acid chloride is attached to a cyclic can be named as :***

IUPAC name of acid chloride in which carbonyl group of acid is attached with cyclic ring :

Cycloalkane Carbonyl chloride

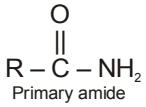
For example,



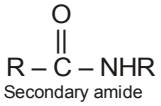
Cyclohexane Carbonyl chloride

Nomenclature of Amides

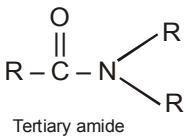
Amides are classified as primary, secondary or tertiary, depending on the number of alkyl group bonded to the nitrogen atom. Primary amides have no alkyl groups bonded to nitrogen, secondary amides have one and teritary amide have two.



Primary amide

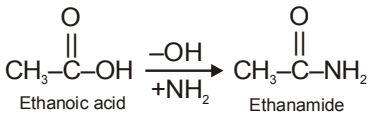


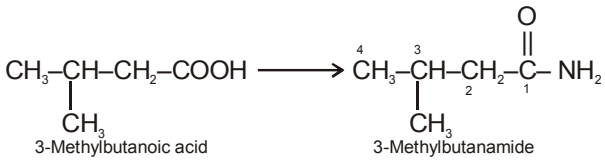
Secondary amide



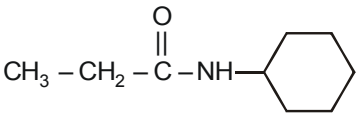
Tertiary amide

(A) **Primary Amides :** Primary amides are named by using the acid name, replacing **oic acid** with **amide.** Thus the general name is Alkanamide, Alkenamide and Alkynamide.

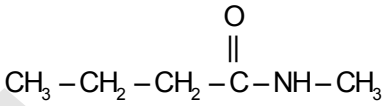




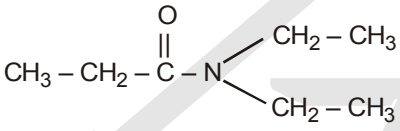
(B) **Secondary and Tertiary amides :** In these two amide, the name of the substituents are indicated first, followed by the name of the amide. The name of each substituent is preceded by a capital N to indicate that the substituent is bonded to a nitrogen. Substituent present on nitrogen are arranged alphabetically.



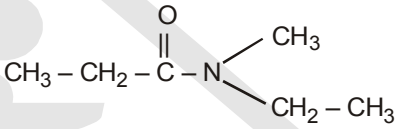
N-cyclohexylpropanamide



N – Methylbutanamide

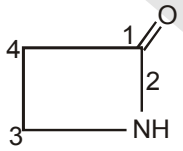


N,N-Diethylpropanamide

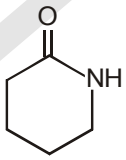


N-Ethyl-N-methylpropanamide

Note : 1 : Cyclic amides are called **lactams.** The IUPAC system name these compounds as Azacycloalkanone

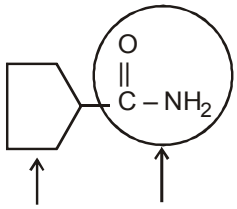


2-Azacyclobutanone



2-Azacyclohexanone

Note : 2 Acid amide in which carbonyl group is attached to the cyclic system can be named as Cycloalkane carboxamide

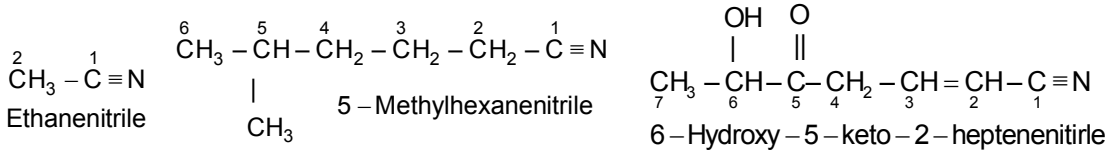


Cyclo alknae Carboxamide
i.e., Cyclopentane

Thus the name is Cyclopentane carboxamide.

NOMENCLATURE OF CYANIDES

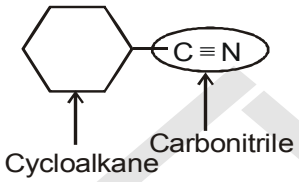
Nitriles are compounds that contain a $-C\equiv N$ functional group. They are considered to the carboxylic acid derivatives because they react with water to form carboxylic acids like acid chlorides, esters and amides. In IUPAC nomenclature nitriles are named by adding nitrile to the hydrocarbon name, i.e., Alkanentrile, Alkenenitrile, Alkynenitrile,



Note : *Nitrile in which cyano group is bonded to a cyclic system can be named as follows :*

(a) **IUPAC Nomenclature of cyanide in which carbon of cyano group is attached with cyclic ring :** The name of such compounds one cyclo alkane carbonitrile

For example,



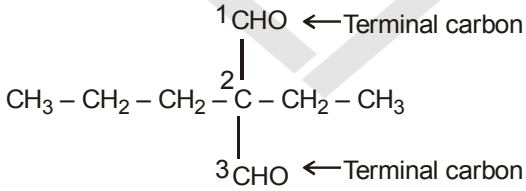
The name is thus Cyclohexane carbonitrile

NOMENCLATURE OF COMPOUNDS HAVING TWO OR MORE LIKE CHAIN TERMINATING PRINCIPAL FUNCTIONAL GROUPS, (Such as –CHO, –COOH, –COCl, – COOR, – $CONH_2$ and –CN)

IUPAC NOMENCLATURE

(1) If compound has only two such functional groups then carbon of one group will be one terminal carbon and carbon of the other functional group be other terminal carbon of the principal chain.

For example :

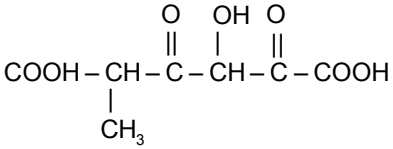


(i) Three carbon chain : Prop.

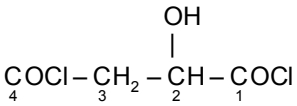
(ii) Two same principal functional group : Alkanedial, i.e., Propanedial.

(iii) Two substituents at carbon-2 of the principal chain i.e., ethyl and propyl.

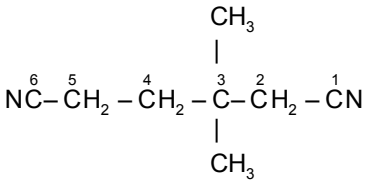
The name of the compound is : 2-Ethyl-2-propylpropanedial



3-Hydroxy-2,4-diketo-5-methylhexanedioic acid



2-Hydroxybutanedioyl chloride



3,3-Dimethylhexanedinitrile

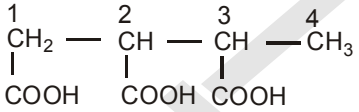
(2) If compound has more than two like groups then two functional groups are treated as principal functional groups.

(i) Carbon of the functional group/groups is not included in the longest possible chains.

(ii) All functional groups having highest priority should be treated as principal functional groups.

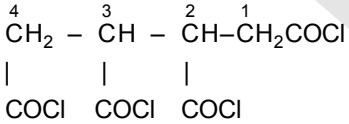
(iii) Compound is always treated as derivative of hydrocarbon.

(1)



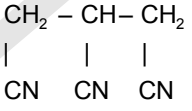
the name is 1,2,3-butanetricarboxylic acid or Butane-1,2,4-tricarboxylic acid

(2)



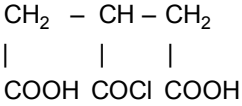
Butane – 1,2,3,4, tetra carbonyl chloride

(3)



1,2,3 – Propanetricarbonitrile

(4)

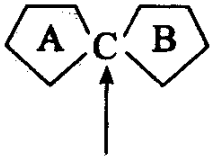


3-Chloroformyl Pentane-1,5-di oic acid

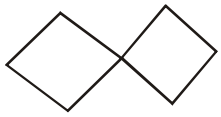
BICYCLIC COMPOUNDS

Bicyclic compounds are compounds that contain two rings.

(i) If the two rings share one carbon, the compound is a spirocyclic compound or simply spiro compound. For example :



This carbon is part of ring A as well as ring B.

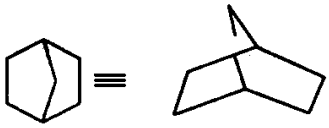


Spirocyclic compound

(ii) If the two rings share two adjacent carbons, the compound is a fused bicyclic compound.

Bicyclic compounds

(iii) If the two rings share more than two carbons, the compound is a bridged bicyclic compound.

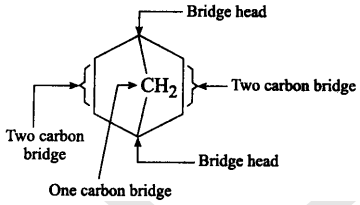


Bicyclic compound

- **IUPAC Nomenclature of Bicyclic Compounds**

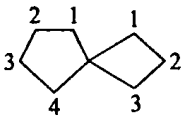
(i) Bicyclic compounds are named by using the alkane name to designate the total number of carbons and the prefix bicyclo or spiro to indicate the number of shared carbons.

(ii) Prefix spiro indicates one shared carbon and bicyclo indicates two or more shared carbons. The following compound, for example, contains seven carbon atoms and is therefore, a bicycloheptane.

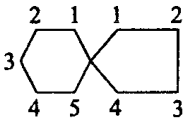


The carbon atoms common to both rings (Number of such carbons is either one in spiro or two in bicyclic) are called bridgeheads and each carbon chain of atoms, connecting the bridgehead atoms is called a bridge.

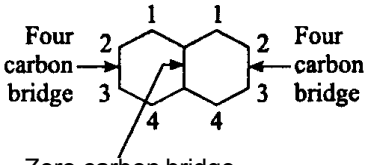
(iii) After the prefix spiro or bicyclic come brackets that contain numbers indicating the number of carbons in each bridge. These are listed in order of decreasing bridge length. For example.



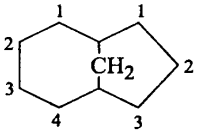
Spiro [3,4] octane



Spiro [4,5] decane



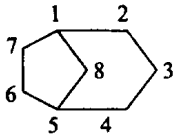
Zero carbon bridge
Bicyclo [4,4,0] decane



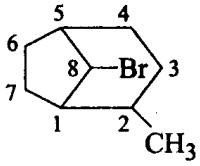
Bicyclo [4, 3, 1] decane

Bicyclo [2, 2, 1] heptane

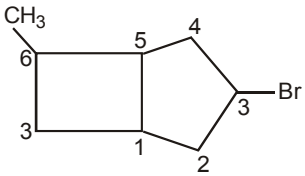
(iv) Numbering in bicyclic compounds starts at any one bridgehead carbon and moves along the longest carbon bridge to the next bridgehead carbon. Continue along the next longest carbon bridge to return to the first bridgehead carbon so that the shortest bridge is numbered last.



Bicyclo [3, 2, 1] octane



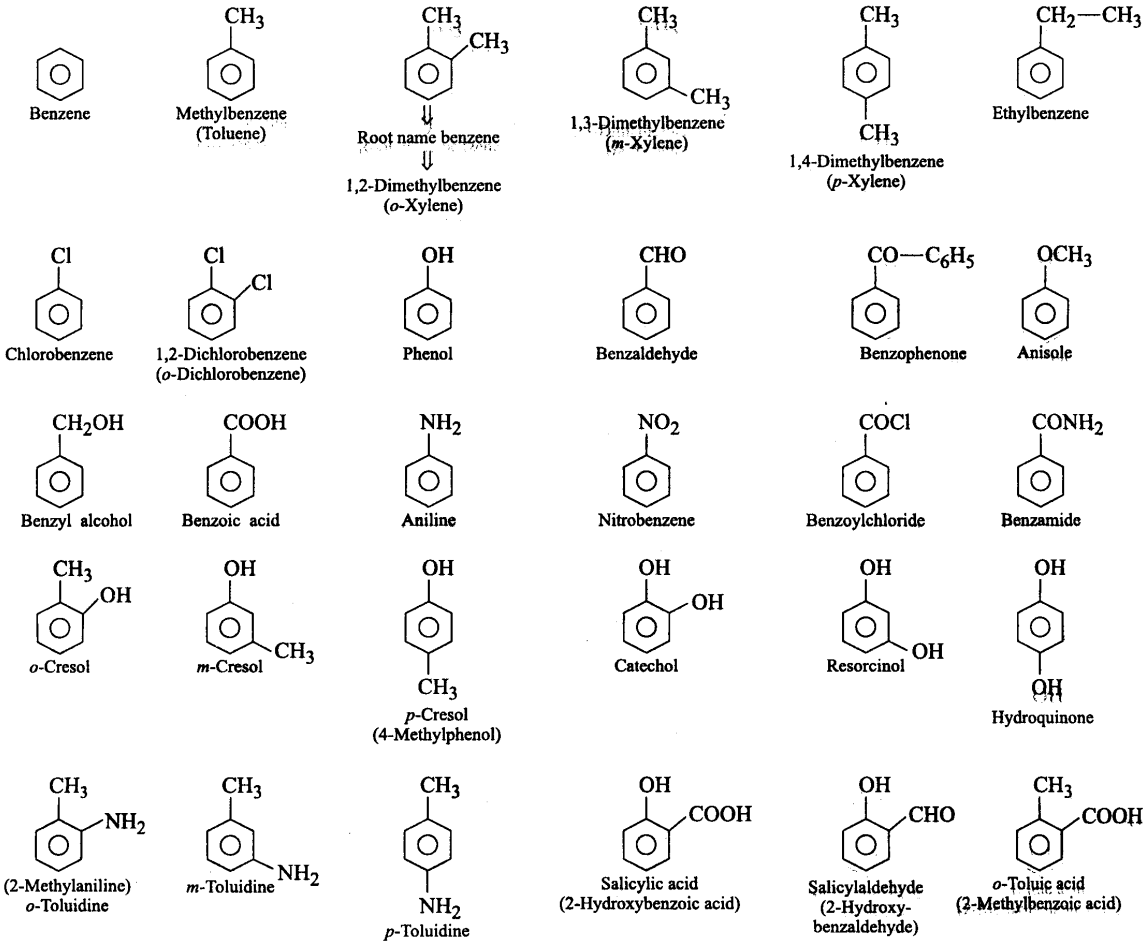
8-Bromo-2-methylbicyclo [3, 2, 1] octane



3-Bromo-6-methylbycyclo[2.3.0] heptane

NOMENCLATURE OF AROMATIC COMPOUNDS

The common names of most of the aromatic compounds are accepted as their IUPAC names. The derivatives of these compounds have their roots derived from the name's of these compounds.



Exercise - I (Only one option is correct)

1. How many 1° carbon atom will be present in a simplest hydrocarbon having two 3° and one 2° carbon atom ?
(A) 3 (B) 4
(C) 5 (D) 6

Sol.

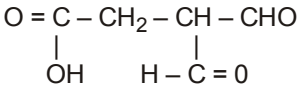
2. $C_3H_6Br_2$ can shows :
(A) Two gem dibromide
(B) Three vic dibromide
(C) Two tert. dibromo alkane
(D) Two sec. dibromo alkane

Sol.

3. The IUPAC name of the compound $CH_3CH = CHCH = CHC \equiv CCH_3$ is :
(A) 4,6-octadiene-2-yne
(B) 2, 4-octadiene-6-yne
(C) 2-octyn-4, 6-diene
(D) 6-octyn-2, 4-diene

Sol.

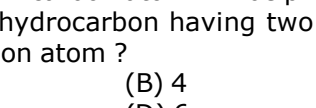
4. The correct IUPAC name of the following compound is :



(A) 3,3-diformyl propanoic acid
(B) 3-formyl-4-oxo-butanoic acid
(C) 3,3-dioxo propanoic acid
(D) 3,3-dicarbaldehyde propanoic acid

Sol.

5. The correct IUPAC name of compound :



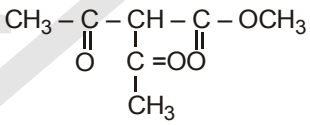
is :
(A) 2-cyano-3-oxopentanal
(B) 2-formyl-3-oxopentanenitrile
(C) 2-cyano-1,3-pentanedione
(D) 1,3-dioxo-2-cyanopentane

Sol.

6. All the following IUPAC name are correct except :
(A) 1-chloro-1-ethoxy propane
(B) 1-amino-1-ethoxypropane
(C) 1-ethoxy-2-propanol
(D) 1-ethoxy-1-propanamine

Sol.

7. IUPAC name of :

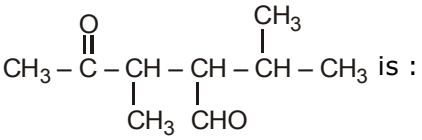


(A) Methyl-2, 2 acetyl ethanoate
(B) 2,2 acetyl-1-methoxy ethanone
(C) Methyl-2-acetyl-3-oxobutanoate
(D) None

Sol.

8. The IUPAC name of β-ethoxy-α-hydroxy propionic acid (trivial name) is :
(A) 1,2-dihydroxy-1-oxo-3-ethoxy propane
(B) 1-carboxy-2-ethoxy ethanol
(C) 3-Ethoxy-2-hydroxy propanoic acid
(D) All above

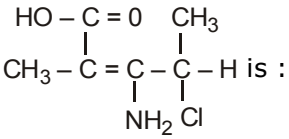
9. The IUPAC name of compound



(A) 3,5-Dimethyl-4-Formyl pentanone
(B) 1-Isopropyl-2-methyl-4-oxo butanal
(C) 2-Isopropyl-3-methyl-4-oxo pentanal
(D) None of the above

Sol.

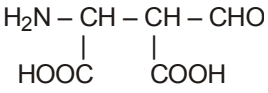
10. The IUPAC name of compound



(A) 2-amino-3-chloro-2-methyl-2-pentenoic acid
(B) 3-amino-4-chloro-2-methyl-2-pentenoic acid
(C) 4-amino-3-chloro-2-methyl-2-pentenoic acid
(D) All of the above

Sol.

11. The IUPAC name of the structure is :



(A) 3-amino-2-formyl butane-1, 4-dioic acid
(B) 3-amino-2, 3-dicarboxy propanal
(C) 2-amino-3-formyl butane-1, 4-dioic acid
(D) 1-amino-2-formyl succinic acid

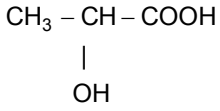
Sol.

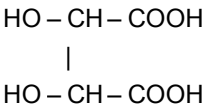
12. How many carbons are in simplest alkyne having two side chains ?

(A) 5 (B) 6
(C) 7 (D) 8

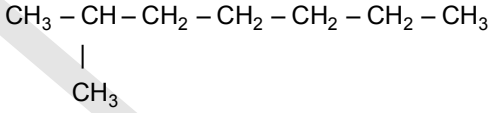
Sol.

13. Which of the following is not correctly matched :

(A) Lactic acid 

(B) Tartaric acid 

(C) Pivaldehyde $CH_3C(CH_3)_2CHO$
(D) Iso-octane



Sol.

14. Which of the following pairs have absence of carbocyclic ring in both compounds ?

(A) Pyridine, Benzene
(B) Benzene, Cyclohexane
(C) Cyclohexane, Furane
(D) Furane, Pyridine

Sol.

15. The commerical name of trichloroethene is :

(A) Westron (B) Perclene
(C) Westrosol (D) Orlone

Sol.

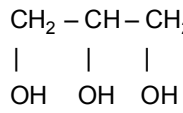
16. The compound which has one isopropyl group is :
(A) 2,2,3,3-tetramethyl pentane
(B) 2,2-dimethyl pentane
(C) 2,2,3-trimethyl pentane
(D) 2-methyl pentane

Sol.

17. How many secondary carbon atoms does methyl cyclopropane have ?
(A) None (B) One
(C) Two (D) Three

Sol.

18. The IUPAC name of the compound



(A) 1,2,3-tri hydroxy propane
(B) 3-hydroxy pentane-1,5 diol
(C) 1,2,3-hydroxy propane
(D) Propane-1,2,3-triol

Sol.

19. As per IUPAC rules, which one of the following groups, will be regarded as the principal functional group?
(A) $-C\equiv C-$ (B) $-OH$
(C) $-\overset{\overset{O}{\|}}{C}-$ (D) $-\overset{\overset{O}{\|}}{C}-H$

Sol.

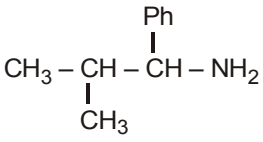
20. Which of the following is the first member of ester homologous series ?
(A) Ethyl ethanoate
(B) Methyl ethanoate
(C) Methyl methanoate
(D) Ethyl methanoate

Sol.

21. The correct IUPAC name of 2-ethyl-3-pentyne is :
(A) 3-methyl hexyne-4
(B) 4-ethyl pentyne-2
(C) 4-methyl hexyne-2
(D) None of these

Sol.

22. The IUPAC name of the compound is



(A) 1-amino-1-phenyl-2-methyl propane
(B) 2-methyl-1-phenyl propane-1-amine
(C) 2-methyl-1-amino-1-phenyl propane
(D) 1-isopropyl-1-phenyl methyl amine

Sol.

23. Which of the following compound is wrongly named ?

(A) $CH_3CH_2CH_2\underset{\underset{Cl}{|}}{C}HCOOH$;

2-Chloro pentanoic acid

(B) $CH_3C \equiv \underset{\underset{CH_3}{|}}{C}CHCOOH$;

2-Methyl hex-3-enoic acid

(C) $CH_3CH_2CH = CHCOCH_3$;

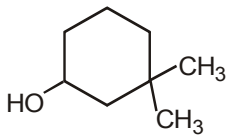
Hex - 3 - en - 2- one

(D) $CH_3 - \underset{\underset{CH_3}{|}}{C}HCH_2CH_2CHO$;

4-Methyl pentanal

Sol.

24. The IUPAC name of the given compound is :



(A) 1,1-dimethyl-3-hydroxy cyclohexane
(B) 3,3-dimethyl-1-hydroxy cyclohexane
(C) 3,3-dimethyl-1-cyclohexanol
(D) 1,1-dimethyl-3-cyclohexanol

Sol.

25. The IUPAC name of $(C_2H_5)_2\ NCH_2\underset{\underset{Cl}{|}}{C}H.COOH$ is

(A) 2-chloro-4-N-ethylpentanoic acid
(B) 2-chloro-3-(N,N-diethyl amino) - propanoic
(C) 2-chloro-2-oxo diethylamine
(D) 2-chloro-2-carboxy-N-ethyl ethane

Sol.

26. The IUPAC name of the compound Br(Cl) Cl. CF_3 is

(A) 2-bromo-2-chloro-2-iodo 1,1,1-trifluoroethane
(B) 1,1,1-trifluoro-2-bromo-2-chloro-2-iodo ethane
(C) 2-bromo-2-chloro-1,1,1-trifluoro-2-iodo ethane
(D) 1-bromo-1-chloro-2,2,2-trifloro-1-iodo ethane

Sol.

27. The group of hetrocylic compounds is :

(A) Phenol, Furane
(B) Furane, Thiophene
(C) Thiophene, Phenol
(D) Furane, Aniline

Sol.

28. The correct IUPAC name of

$CH_3 - CH_2 - \underset{\underset{CH_2}{||}}{C} - COOH$ is :

(A) 2-methyl butanoic acid
(B) 2-ethyl-2-propenoic acid
(C) 2-carboxy-1-butene
(D) None of the above

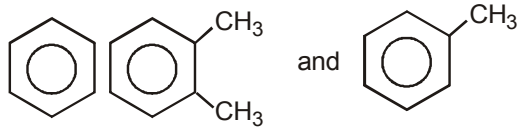
Sol.

29. The IUPAC name of the following structure $(CH_3)C.C.C.(CH_3)CH(CH_3)$ is :
(A) 3-methyl-4-hexynene-2
(B) 3-methyl-2-hexenyne-4
(C) 4-methyl-4-hexenyne-4
(D) all are correct

Sol.

30. The IUPAC name of the following structure is $[CH_3CH(CH_3)]_2\ C(CH_2CH_3)C(CH_3)C(CH_2CH_3)_2$
(A) 3,5-diethyl-4,6-dimethyl-5-[1-methylethyl]-3-heptene
(B) 3,5-diethyl-5-isopropyl-4,6-dimethyl-2-heptene
(C) 3,5-diethyl-5-propyl-4,6-dimethyl -3-heptene
(D) None of these

Sol.

31. 

Number of secondary carbon atoms present in the above compounds are respectively :
(A) 6,4,5 (B) 4, 5, 6
(C) 5,4,6 (D) 6,2,1

Sol.

32. The IUPAC name of acetyl acetone is :
(A) 2,5-Pentane dione
(B) 2,4-Pentane dione
(C) 2,4-Hexane dione
(D) 2,4-butane dione

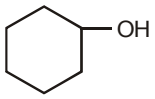
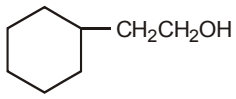
Sol.

33. When vinyl & allyl are joined each other, we get
(A) Conjugated alkadiene
(B) comulative alkadiene
(C) Isolated alkadiene
(D) Allenes

Sol.

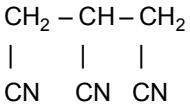
34. Glycerine is :
(A) Propane triol-1,2,3
(B) Propylene trialcohol
(C) Propyl glycol
(D) Hydroxy methyl glycol

Sol.

35. (a)  and (b) 

True statement for the above compounds is
(A) (a) is phenol while (b) is alcohol
(B) Both (a) and (b) are primary alcohol
(C) (a) is primary and (b) is secondary alcohol
(D) (a) is secondary and (b) is primary alcohol

Sol.

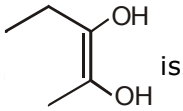
36. IUPAC name will be 

(A) 1,2,3-Tricyano propane
(B) Propane trinitrile-1,2,3
(C) 1,2,3-cyano propane
(D) Propane-1,2,3-tricarbonitrile

Sol.

37. A substance containing an equal number of primary, secondary and tertiary carbon atoms is :
(A) Mesityl Oxide (B) Mesitylene
(C) Maleic acid (D) Malonic acid

Sol.

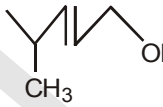
38. IUPAC name of  is

(A) But-2-ene-2, 3-diol
(B) Pent-2-ene-2, 3-diol
(C) 2-methylbut-2, ene-2,3-diol
(D) Pent-3-ene-3, 4-diol

Sol.

39. The IUPAC name of
$BrCH_2 - \underset{\displaystyle CONH_2}{\underset{|}{CH}} - CO - CH_2 - CH_2CH_3$ is :
(A) 2-bromo methyl-3-oxo hexanamide
(B) 1-bromo-2-amino-3-oxo hexane
(C) 1-bromo - 2- amino-n-propyl ketone
(D) 3-bromo-2-propyl propanamide

Sol.

40. IUPAC name of  is :

(A) 5-methyl hexanol
(B) 2-methyl hexanol
(C) 2-methyl hex-3-enol
(D) 4-methyl pent-2-en-1-ol

Sol.

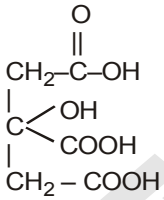
41. The IUPAC name of $CH_3CH_2 - \underset{\displaystyle CH_3}{\underset{|}{N}} - CH_2CH_3$ is
(A) N-methyl-N-ethyl ethanamine
(B) diethyl methanamine
(C) N-ethyl-N-methyl ethanamine
(D) methyl diethyl ethanamine

Sol.

42. The molecular formula of the first member of the family of alkenynes and its name is given by the set

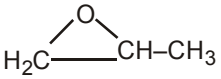
(A) C_3H_2, alkene
(B) C_5H_6, 1-penten-3-yne
(C) C_6H_8, 1-hexen-5-yne
(D) C_4H_4, butenyne

Sol.

43. The IUPAC name of compound 

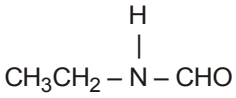
(A) 1,2,3-tricarboxy-2-propanol
(B) 2-hydroxy propane-1,2,3 tricarboxylic acid
(C) 3-hydroxy-3-Carboxy, 1,5-pentane dioic acid
(D) None

Sol.

44. The IUPAC name of the compound : 

(A) Propylene Oxide
(B) 1,2-Oxo propane
(C) 1,2-Epoxy propane
(D) 1,2-Propoxide

Sol.

45. One among the following is the correct IUPAC name of the compound 

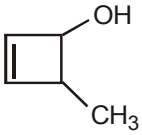
(A) N-Formyl aminoethane
(B) N-Ethyl formyl amine
(C) N-Ethyl methanamide
(D) Ethylamino methanal

Sol.

46. Which among the following is the correct IUPAC name of isoamylene :

(A) 1-Pentene
(B) 2-Methyl-2-butene
(C) 3-Methyl-1-butene
(D) 2-Methyl-1-butene

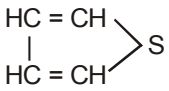
Sol.

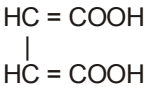
47. The IUPAC name of  is

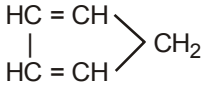
(A) 3-Methyl cyclo-1-butene-2-ol
(B) 4-Methyl cyclo-2-butene-1-ol
(C) 4-Methyl cyclo-1-butene-3-ol
(D) 2-Methyl cyclo-3-butene-1-ol

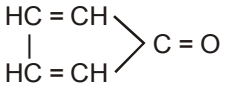
Sol.

48. Which of the following is a heterocyclic compound

(A) 

(B) 

(C) 

(D) 

Sol.

49. The number of primary, secondary and tertiary amines possible with the molecular formula C_3H_9N is :

(A) 1, 2 , 2 (B) 1, 2, 1
(C) 2,1,1 (D) 3, 0, 1

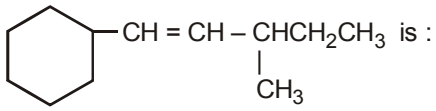
Sol.

50. The IUPAC name of $C_6H_5CH = CH - COOH$ is :

(A) cinnamic acid
(B) 1-phenyl-2-carboxy ethane
(C) 3-phenyl prop-2-enoic acid
(D) dihydroxy-3-phenyl propionic acid.

Sol.

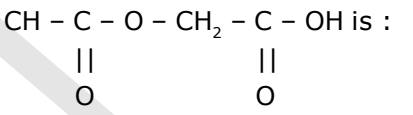
51. The IUPAC name of

 is :

(A) 1-cyclohexyl-3-methyl-1-pentene
(B) 3-methyl-5-cyclohexyl-pent-ene
(C) 1-cyclohexyl-3-ethyl-but-1-ene
(D) 1-cyclohexyl-3, 4-dimethyl-but-1-ene

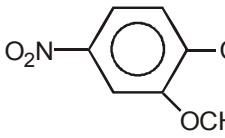
Sol.

52. The IUPAC name of

 is :

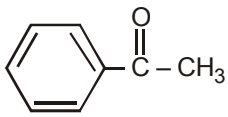
(A) 1-acetoxy acetic acid
(B) 2-acetoxy ethanoic acid
(C) 2-ethanoyl oxyacetic acid
(D) 2-ethanoyl oxyethanoic acid

Sol.

53. The IUPAC name of  is

(A) 2-methoxy-4-nitro benzaldehyde
(B) 4-nitro anisaldehyde
(C) 3-methoxy-4-formyl nitro benzene
(D) 2-formyl-4-nitro anisole

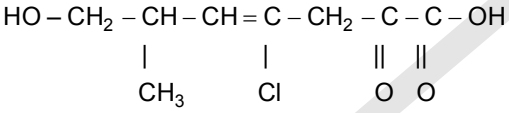
Sol.

54. The IUPAC name of  is :

(A) phenyl ethanone
(B) methyl phenyl ketone
(C) acetophenone
(D) phenyl emethyl ketone

Sol.

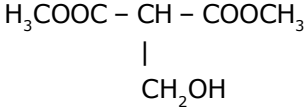
55. The suffix of the principal group, the prefixes for the other groups and the name of the parent in the structure



(A) -oic acid, chloro, hydroxy, oxo, methyl, 4-heptene
(B) -oic acid, chloro, hydroxy, methyl, oxo, 4-heptene
(C) -one carboxy chloro. methyl, hydroxy, 4-heptene
(D) -one, carboxy, chloro, methyl, hydroxy, 4-heptene

Sol.

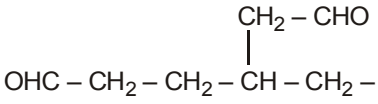
56. The IUPAC name of compound



(A) 2-hydroxy methyl methyl propandioate
(B) Methyl-2-hydroxy methyl propandioate
(C) dimethyl-2-hydroxy methyl propandioate
(D) 2-hydroxy methyl - dimethyl propandioate

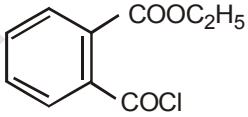
Sol.

57. The IUPAC name of



(A) 4,4-di (formylmethyl) butanal
(B) 2-(formylmethyl) butane-1,4-dicarbaldehyde
(C) hexane-3-acetal-1, 6-dial
(D) 3-(formylmethyl) hexane-1, 6-dial

Sol.

58. The IUPAC name of  is :

(A) 2-chlorocarbonyl ethylbenzoate
(B) 2-carboxyethyl benzoyl chloride
(C) ethyl-2-(chlorocarbonyl) benzoate
(D) ethyl-1-(chlorocarbonyl) benzoate

Sol.

59. Which of the following is crotonic acid :

(A) $CH_2 = CH - COOH$
(B) $C_6H_5 - CH = CH - COOH$
(C) $CH_3 - CH = CH - COOH$
(D) CH – COOH
||
CH – COOH

Sol.

60. $CH_3 - O - \underset{\underset{O}{\|}}{C} - CH_2 - COOH$

The correct systematic name of the above compound is :

(A) 2-acetoxy ethanoic acid
(B) 2-methoxy carbonyl ethanoic acid
(C) 3-methoxy formyl ethanoic acid
(D) 2-methoxy formyl acetic acid

Sol.

61. Structural formula of isopropyl methanoate is :

(A) $CH_3 - \underset{\underset{O}{\|}}{C} - O - \underset{\underset{CH_3}{|}}{CH} - CH_3$

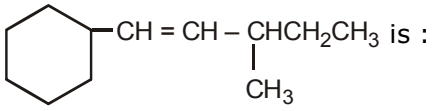
(B) $H - \underset{\underset{O}{\|}}{C} - O - \underset{\underset{CH_3}{|}}{CH_2} - CH_3$

(C) $CH_3 - \underset{\underset{O}{\|}}{C} - O - CH_2 - \underset{\underset{CH_3}{|}}{CH_2}$

(D) $H - \underset{\underset{O}{\|}}{C} - O - \underset{\underset{CH_3}{|}}{CH} - CH_3$

Sol.

62. The IUPAC name of

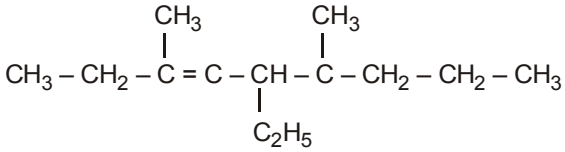


is :

(A) 1-cyclohexyl-3-methyl-1-pentene
(B) 3-methyl-5-cyclohexyl-pent-1-ene
(C) 1-cyclohexyl-3-ethyl-but-1-ene
(D) 1-cyclohexyl-3, 4-dmethyl-but-1-ene

Sol.

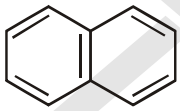
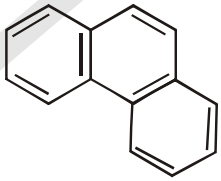
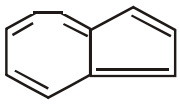
63. The correct IUPAC name of the compound



(A) 5-ethyl-3, 6-dimethyl non-3-ene
(B) 5-ethyl-4, 7-dimethyl non-3-ene
(C) 4-methyl-5, 7-diethyl oct-2-ene
(D) 2,4-ethyl-5-methyl oct-2-ene

Sol.

64.

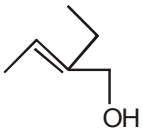
Column-I		**Column - II**
(A)		(P) Phenanthrene
(B)		(Q) Anthracene
(C)		(R) Azulene
(D)		(S) Napthalene

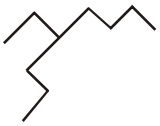
Sol.

Exercise - II (Subjective Problems)

Give the IUPAC name for each of the following :

Give the IUPAC name for each of the following :

1. 

2. 

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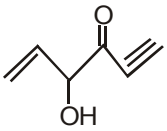
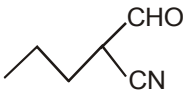
4. 

5. 

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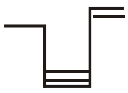
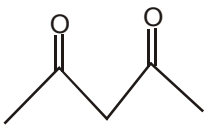
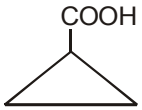
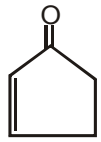
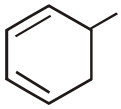
7. 

8. 

9. 

10. 

11. 

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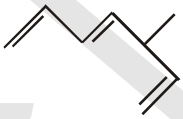
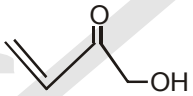
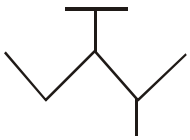
13. 

14. 

15. 

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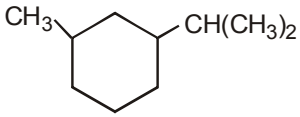
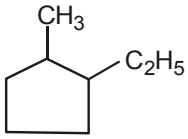
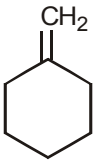
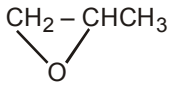
17. 

18. 

19. 

20. 

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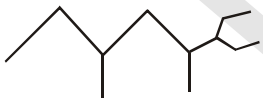
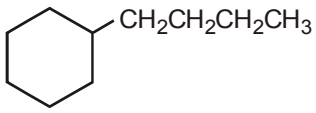
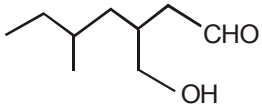
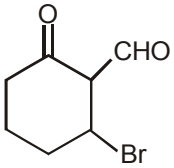
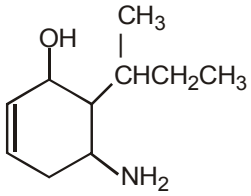
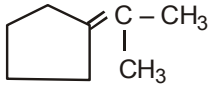
22. 

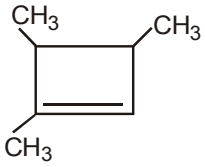
23. 

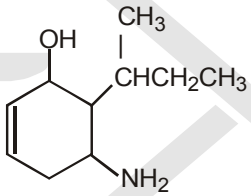
24. 

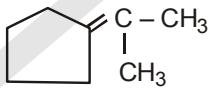
25. 

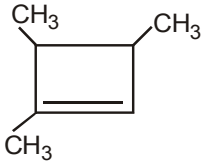
26. 

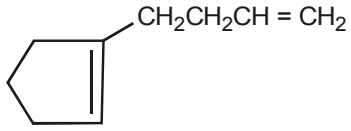
27. 

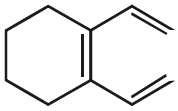
28. 

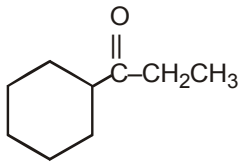
26. 

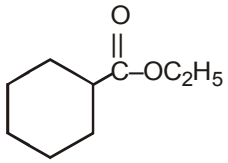
27. 

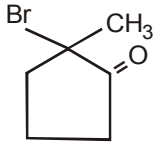
28. 

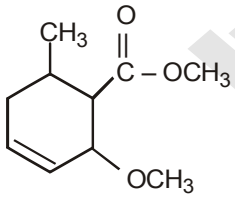
29. 

30. 

31. 

32. 

33. 

34. 

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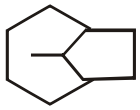
36. 

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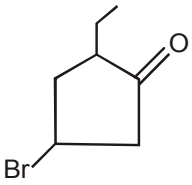
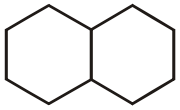
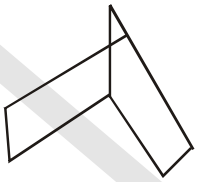
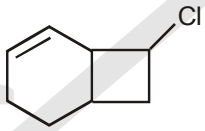
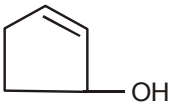
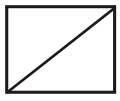
39. 

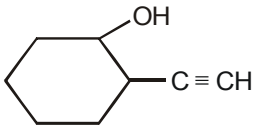
40. 

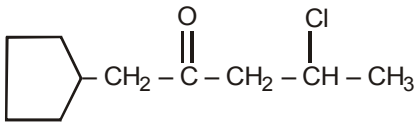
41. 

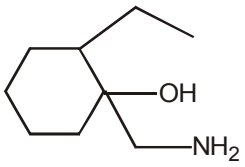
42. 

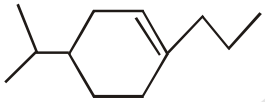
43. 

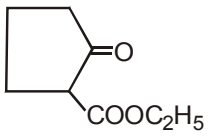
44. 

45. 

46. 

47. 

48. 

49. 

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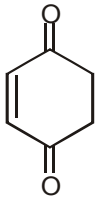
51. 

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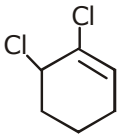
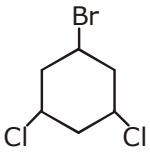
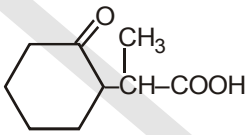
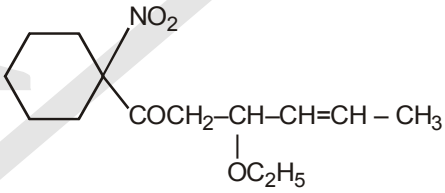
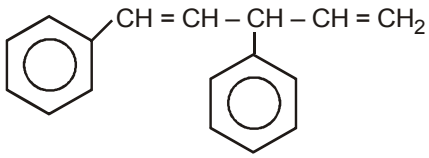
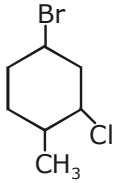
53. 

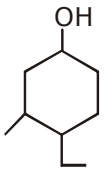
54. 

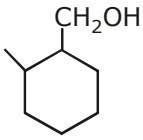
55. 

56. 

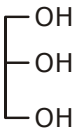
57. 

58. 

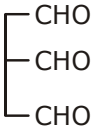
59. 

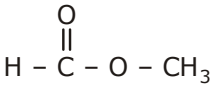
60. 

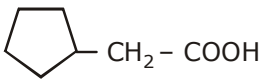
61. 

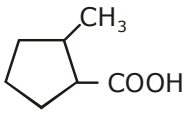
62. 

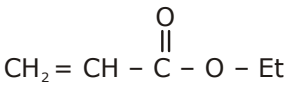
63. 

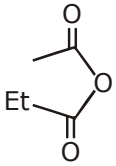
64. 

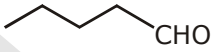
65. 

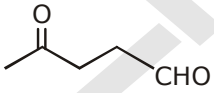
66. 

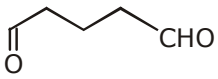
67. 

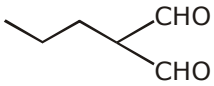
68. 

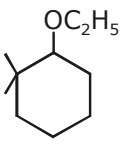
69. 

70. 

71. 

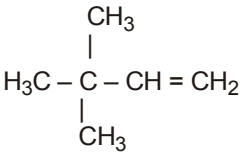
72. 

73. 

74. 

Exercise - III (Jee Problems)

Q.1 The IUPAC name of the compound having the formula is :



(A) 3,3,3-trimethyl-1-propene
(B) 1,1,1-trimethyl-2-propene
(C) 3,3-dimethyl-1-butene
(D) 2,2-dimethyl-3-butene **[JEE 1984]**

Sol.

Q.2 Write the IUPAC name of $CH_3CH_2CH{=}CH.COOH$ **[JEE 1986]**

Sol.

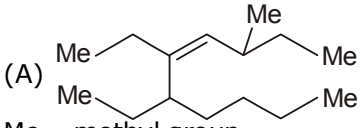
Q.3 The IUPAC name of the compound $CH_2 = CH - CH(CH_3)_2$ is :
(A) 1,1-dimethyl-2-propene
(B) 3-methyl-1-butene
(C) 2-vinyl propane
(D) None of the above **[JEE 1987]**

Sol.

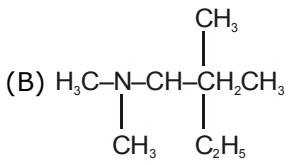
Q.4 The number of sigma and pi-bonds in 1-butene 3-yne are :
(A) 5 sigma and 5 pi
(B) 7 sigma and 3 pi
(C) 8 sigma and 2 pi
(D) 6 sigma and 4 pi **[JEE 1989]**

Sol.

Q.5 Write IUPAC name of following :



Me = methyl group



[JEE 1991]

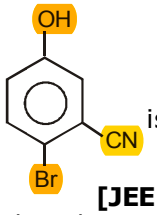
Sol.

Q.6 Write IUPAC name of succinic acid. **[JEE 1994]**

Sol.

Q.7 The IUPAC name of C_6H_5COCl is
(A) Benzoyl chloride
(B) Benzene chloro ketone
(C) Benzene carbonyl chloride
(D) Chloro phenyl ketone **[JEE 2006]**

Sol.

Q.8 The IUPAC name of  is :

[JEE 2009]

(A) 4-Bromo-3-cyanophenol
(B) 2-Bromo-5-hydroxybenzonitrile
(C) 2-Cyano-4-hydroxybromobenzene
(D) 6-Bromo-3-hydroxybenzonitrile

Sol.

Q.9 The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was: **[IIT Mains 2013]**
(A) Phosgene (B) Methylisocynate
(C) Methylamine (D) Ammonia

Sol.

ANSWER-KEY

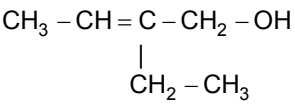
Exercise-I

Q.1	B	**Q.2**	A	**Q.3**	B	**Q.4**	B	**Q.5**	B	**Q.6**	B	**Q.7**	C
Q.8	C	**Q.9**	C	**Q.10**	B	**Q.11**	C	**Q.12**	B	**Q.13**	D	**Q.14**	D
Q.15	C	**Q.16**	D	**Q.17**	C	**Q.18**	D	**Q.19**	D	**Q.20**	C	**Q.21**	C
Q.22	B	**Q.23**	B	**Q.24**	C	**Q.25**	B	**Q.26**	D	**Q.27**	B	**Q.28**	B
Q.29	B	**Q.30**	A	**Q.31**	A	**Q.32**	B	**Q.33**	C	**Q.34**	A	**Q.35**	D
Q.36	D	**Q.37**	B	**Q.38**	B	**Q.39**	A	**Q.40**	D	**Q.41**	C	**Q.42**	D
Q.43	B	**Q.44**	C	**Q.45**	C	**Q.46**	C	**Q.47**	B	**Q.48**	A	**Q.49**	C
Q.50	C	**Q.51**	A	**Q.52**	D	**Q.53**	A	**Q.54**	A	**Q.55**	B	**Q.56**	B
Q.57	D	**Q.58**	C	**Q.59**	C	**Q.60**	B	**Q.61**	D	**Q.62**	A	**Q.63**	A

Q.64 (A) – Q, **(B)** – S, **(C)** – P, **(D)** – R

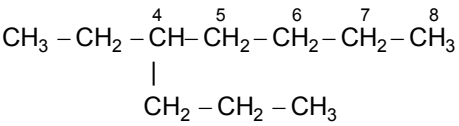
Exercise-II

Q.1

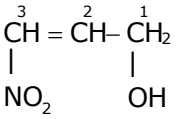


2-ethyl-2-buten-1-ol

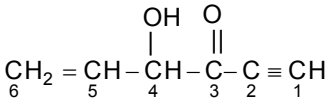
Q.2



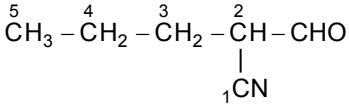
4-Ethyl octane

Q.3 

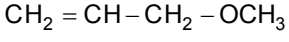
3-nitro-2-propen-1-ol

Q.4 

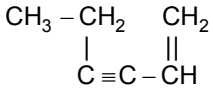
4-hydroxy-5-hexen-1yn-3-one

Q.5 

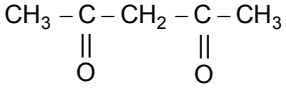
2-formyl pentane nitrile

Q.6 

3-Methoxy-1-propene

Q.7 

1-Hexen-3-yne

Q.8 

2-4,pentane dione

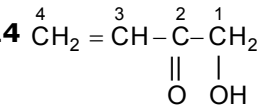
Q.9 Cyclopropanecarboxylic acid

Q.10 Cyclopent-2-en-1-one

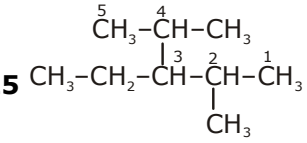
Q.11 5 Methyl cyclohexa-1, 3-diene

Q.12 Cyclopent-2-en-1-one

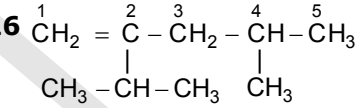
Q.13 5-methyl hepta-1,3,6-triene

Q.14 

1-Hydroxy-3-Buten-2-one
1,3-cyclobutadiene

Q.15 

3-Ethyl-2,4-dimethyl pentane

Q.16 

2-isopropyl-4-methyl-1-pentene
or 4-methyl-2-(methyl ethyl)-1-pentene

Q.17 1-methyl-3-(methyl ethyl) cyclohexane
or 3-isopropyl-1-methylcylohexane

Q.18 1-ethyl-2-methylcyclopentane

Q.19 Methylene cyclohexane

Q.20 1,2-epoxy propane

Q.21 2,2,6,7-tetramethylocatane

Q.22 3-ethyl-4,6-dimethyloctane

Q.23 Butyl cyclohexane

Q.24 3-(hydroxymethyl)-5-methylheptanal

Q.25 2-Bromo-6-oxocyclohexanecarbaldehyde

Q.26 5-amino-6(1-methyl propyl) cyclo-hex-2-enol

Q.27 Isoproylidenecyclopentane

or 1-methyl ethylidene cyclopentane

Q.28 1,3,4-trimethyl-1-cyclobutene

Q.29 1-(3-butenyl) cyclopentene

Q.30 1,2-diethenyl cyclohexene

Q.31 1-cyclohexyl-1-propanone

Q.32 Ethyl cyclohexanecarboxylate

Q.33 2-bromo-2-methyl cyclopentanone

Q.34 Methyl-2-methoxy-6-methyl-3-cyclohexene carboxylate

Q.35 Bicylo (2.2.1) heptane

Q.36 9-methyl bicyclo(4.2.1) nonane

Q.37 spiro (2.5) octane

Q.38 spiro (4.5) decane

Q.39 4-Bromo-2-ethyl cyclopentanone

Q.40 Bicyclo (4.4.0) decane

Q.41 Bicyclo (2.2.1) heptane

Q.42 8-chloro bicyclo(4.2.0) oct-2-ene

Q.43 2-cyclopenten-1-ol

Q.44 Bicyclo (1.1.0) butane

Q.45 2-ethynyl cyclohexanol

Q.46 4-chloro-1-cyclopentyl pentane-2-one

Q.47 1-Amino methyl-2-ethyl cyclohexanol

Q.48 1-propyl-4-isopropyl-1-cyclohexene or 4-(methyl ethyl)-1-propyl cyclohexene

Q.49 Ethyl-2-oxo-cyclo pentane carboxylate

Q.50 Bicyclo (3.1.0) hexane

Q.51 Cyclohex-2-en-1, 4-dione

Q.52 1,4-Dimethyl Cyclobutene

Q.53 1,6-Dichlorocyclohexene

Q.54 1-Bromo-3,5-dichlorocyclohexane

Q.55 2-(2-oxo-cyclohexyl) propanoic acid

Q.56 3-ethoxy-1(1-nitrocyclohexyl)-hex-4-en-1-one

Q.57 1,3-diphenyl-1, 4-pentadiene

Q.58 4-Bromo-2-chloro-1-methyl cyclohexane

Q.59 4-Ethyl-3-methylcyclohexanol

Q.60 1(2-Methylcyclohexyl) methanol

Q.61 Ethane-1,2-diol

Q.62 Propane-1,2,3-triol

Q.63 Butane-1,4-dial

Q.64 Propane-1,2,3-tricarbaldehyde

Q.65 Methyl methanoate

Q.66 2-cyclopentyl ethanoic acid

Q.67 2-Methyl cyclopentane carboxylic acid

Q.68 Ethyl prop-2-enoate

Q.69 Ethanoic propnoic anhydride

Q.70 Pentanal

Q.71 4-Oxopentanal

Q.72 Pentane-1,5-dial

Q.73 2-Propyl propanedial

Q.74 2-ethoxy-1,1-dimethyl cyclohexane

Exercise-III

Q.1 C

Q.2 $\underset{5}{CH_3}-\underset{4}{CH_2}-\underset{3}{CH}=\underset{2}{CH}-\underset{1}{COOH}$

2-pentene, 1-oic acid and or 2-pentenoic acid

Q.3 B **Q.4** B

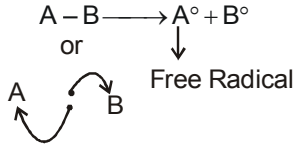
Q.5 (a) 5,6-diethyl-3-methyl-dec-4-ene

(b) N,N, 2,2-tetramethyl-1-butanamine **Q.6** Butane-1, 4-dioic acid

Q.7 C **Q.8** B **Q.9** B

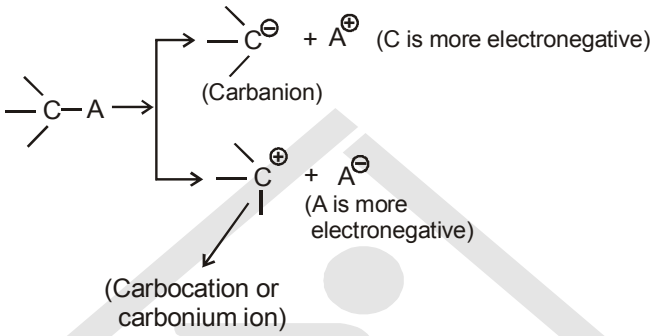
HOMOLYTIC BOND FISSION HOMOLYSIS

The bond cleavage in which each bonded atom gets their own contribution

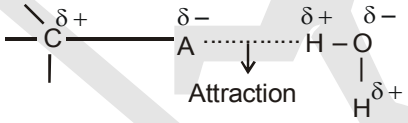


- Cleavage takes place due to
  HELP (H = Heat, E = Electricity, L = light, P = Peroxide)
- Favoured when E.N. difference is less or zero.
- Cleavage favoured in non polar solvent.

HETROLYTIC BOND FISSION



- It is formed when the electronegativity difference between the bonded atoms is more
- formation is favoured by polar solvent



+ve charge of the solvent attracts the –ve pole of compound and the –ve pole of the solvent attracts +ve pole of compound and the bond breaks.

INTERMEDIATES OF ORGANIC COMPOUNDS

		Free Radical	Carbocation	Carbanion
(1)	Lone pair	0	0	1
(2)	Bond pair	3	3	3
(3)	Unpaired e^-	1	×	×
(4)	Bond Angle	120º	120º	107º
(5)	Hybridisation	sp^2	sp^2	sp^3
(6)	Shape	Trigonal planer	Trigonal planer	Pyramidal
(7)	Magnetic property	Paramagnetic	Diamagnetic	Diamagnetic
(8)	Stability order (As per inductive effect)	3º > 2º > 1º	3º > 2º > 1º	1º > 2º > 3º
(9)	e^- rich/deficient/poor	ED(Deficient)	ED	ER(Rich)
(10)	Reactivity order	1º > 2º > 3º	1º > 2º > 3º	3º > 2º > 1º
(11)	+I/–I (stablized)	+I	+I	–I

ELECTRONIC DISPLACEMENT EFFECT

The displacement of electrons within the same molecule is known as electronic displacement. These effects affect the stability of a species or compound and it also affect the acidic & basic strength.

Electronic Displacement Effect is divided into two parts:–

(1) Permanent effect
(2) Temporary effect

(1) Permanent effect

(i) Inductive effect
(ii) Mesomeric (resonance) effect
(iii) Hyperconjugation

(2) Temporary effect:

(i) Electromeric effect
(ii) Inductomeric effect

(i) Inductive effect:

It is an effect in which permanent polarisation arises due to partial displacement of σ-electrons along carbon chain or partial displacement of sigma-bonded electron toward more electronegative atom in carbon chain.

$$\overset{+\delta_3}{C}\rightarrow\overset{+\delta_2}{C}\rightarrow\overset{+\delta_1}{C}\rightarrow\overset{-\delta}{Cl}$$

Magnitude of partial positive charge

$+\delta_1 > +\delta_2 > +\delta_3 = \delta^-$ (net charge remain constant in a molecule having inductive effect)

Inductive effect

It is a permanent effect

$$\overset{5}{C}\overset{\delta\delta\delta+}{\text{—}}\overset{4}{C}\rightarrow\overset{3}{C}\rightarrow\overset{2}{C}\rightarrow\overset{1}{C}\rightarrow X \quad (-I \text{ effect of X})$$

if X i.e more electronegative

(After carbon No. 3 the effect disappears)

$$C\overset{\delta\delta\delta-}{\text{—}}C\overset{\delta\delta-}{\text{—}}C\overset{\delta-}{\text{—}}C\overset{\delta+}{\text{—}}Y \quad (+ \text{ I effect of Y})$$

* $H-\overset{H}{\underset{|}{\overset{|}{\overset{+}{N}}}}-H < R-\overset{R}{\underset{|}{\overset{|}{\overset{\oplus}{N}}}}-R$ (– I effect order)

* $O^- < O < O^+$ (–I effect order)

- It is a permanent effect
- It is caused due to electronegative difference.
- It operates via σ bonded electron.
- It is distance dependent effect.

- As distance increases, its effect decreases.
- It can be negalected after third carbon.
- It is a destablising effect.
- It is divided into 2 parts. (On the basis of electronegativity w.r.t. hydrogen atom)
  (1) +I effect
  (2) – I effect

  If any atom or group having electronegativity greater than that of hydrogen. than it is considered as – I effect and vice-versa.

	+I effect	**– I effect**
(i)	e^- releasing group	(i) e^- accepting group
(ii)	EN less than H	(ii) EN greater than H
(iii)	Those group which are showing + I effect, disperses partial – ve charge on the C-chain	(iii) Those group showing –I effect disperses + ve charge on the C-chain

Eg. $CH_3 - CH_2 - Cl$ (–I of Cl)

Eg. $CH_3 - CH = CH_2$ (–I of $-CH=CH_2$ & +I of $-CH_3$)

Eg. $CH_3 - CH_2 - C \equiv CH$ (–I of $-C \equiv CH$ & + I of $-CH_2-CH_3$)

Eg. I – Cl
+I –I

Eg. $CH_2 = CH$–  (–I of –ph)

Order of –I effect showing group:

$$-\overset{\oplus}{N}F_3 > -\overset{\oplus}{N}R_3 > -\overset{\oplus}{N}H_3 > -NO_2 > -CN > -\overset{O}{\overset{\|}{C}}-H > -\overset{O}{\overset{\|}{C}}-R > -\overset{O}{\overset{\|}{C}}-OH > -F > -Cl > -Br > -I$$

(–I order) $-C \equiv CH > -CH = CH_2$

Order of + I effect showing group

$$-\overset{\ominus}{C}H_2 > -\overset{\ominus}{N}H > -\overset{\ominus}{O} > -CMe_3 > -CHMe_2 > -CH_2Me > CT_3 > CD_3 > CH_3 > T > D > H$$

Bond Strength : $CT_3 > CD_3 > CH_3$ (+ I of T > D > H)

Q. Why carbon - hydrogen bond is longer than C - T bond

Ans. As the mass increases, vibration decreases as a result of which the heavier isotope will be more closer to the C-atom for a longer time. Therefore C – T bond is stronger C – T > C – D > C – H
Which implies that C – H bond has longest bond

APPLICATION OF INDUCTIVE EFFECT

To compare the stability of intermediates.

Intermediates

These are real separable species having measurable stability formed during coversion of reactant to product. (After bond cleavage and before bond formation).

6 types of intermediates:

(i) Free radical (ii) Carbocation (iii) Carbanion

(iv) Carbene (v) Nitrene (vi) Benzyne

They are formed by homolytical and heterolytical cleavage.

MESOMERIC EFFECT (RESONANCE EFFECT)

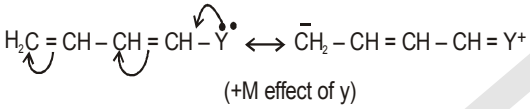
Mesomeric effect is valid only for conjugated system.

Types

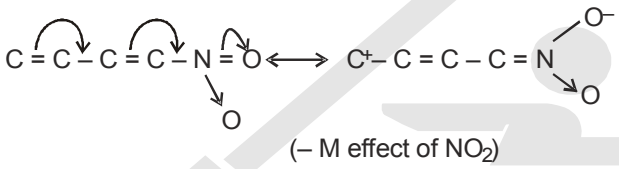
1 + M effect (+R)

2 – M Effect (–R)

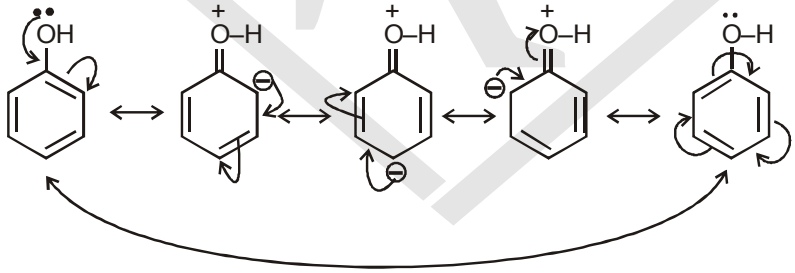
* Consider the following conjugated system



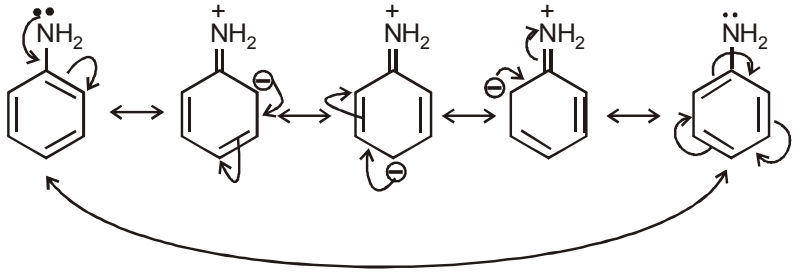
* Consider another conjugated system



MESOMERIC EFFECT IN PHENOL (+ M EFFECT)



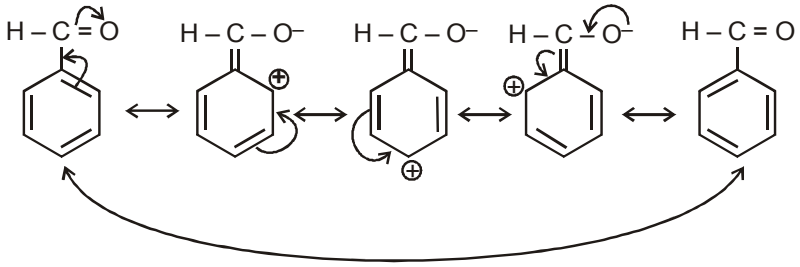
+M effect in aniline



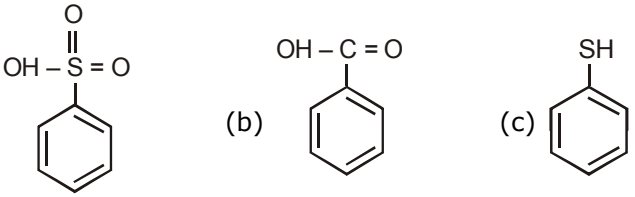
If the movement of e^- is towards ring $\Rightarrow$ (+M effect)

$\Rightarrow$ This effect increases the electron density over benzene ring.

* –M effect in Benzaldehyde



Ex.23 Idenfity the compound showing +M or –M seperately

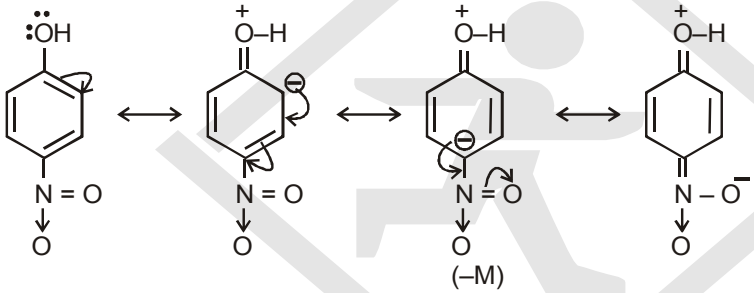


(a) (b) (c)

Sol. (a) (–M) (b) (–M) (c) +M

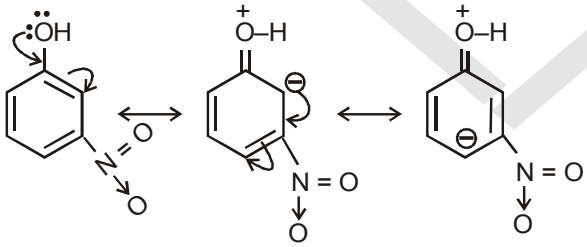
* +M group increases electron density of ring while – M decreases the electron density of benzene ring.

* if NO_2 is present on the ortho or para position then along with its –I effect, It will also show –M effect.



(–M)

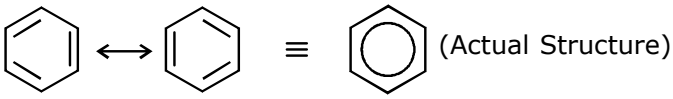
***** Above compound have +M of –OH and –M of NO_2 group.



as we can easily see that $-NO_2$ at meta position is not attracting e^- density towards it self and that's why it will not show –M effect at m-position

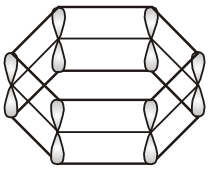
RESONANCE

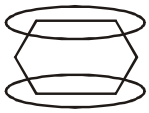
Delocalisation of π-electrons in conjugation is known as resonance.



(Actual Structure)

(resonating structures) (Resonance hybrid)

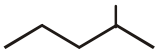


in this form 

CONDITION FOR SHOWING RESONANCE

1. Molecule should be planer, nearly planer or a part of it is planar

Q.1 Which are planer

(A)  (B)  *(C)  *(D) 

Because all carbon atoms are sp^2 hybridised.

2. Molecule should posses conjugated system.

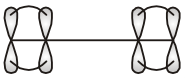
Conjugated system :–

Continuous unhybridised p-orbital parallel to each–other.

Types of conjugated system:–

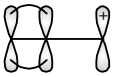
(1) π-bond alternate to π-bond

$CH_2 = CH - CH = CH_2$



(2) π-bond alternate to + charge

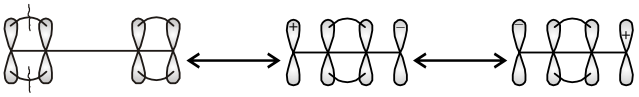
$CH_2 = CH - CH_2^+$



Eg. $CH_2 = \overset{\curvearrowright}{CH} - CH = \underset{\curvearrowright}{CH_2}$

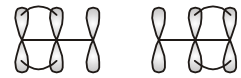
$\overset{\oplus}{C}H_2 - CH = CH - \overset{\ominus}{C}H_2$

$\overset{\ominus}{C}H_2 - CH = CH - \overset{\oplus}{C}H_2$ } R.S. $\equiv CH_2 \cdots CH = CH \cdots CH_2$



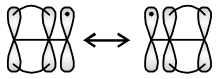
Eg. $CH_2 = CH - \overset{\ominus}{C}H_2$ 

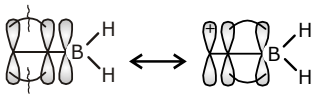
$\overset{\ominus}{C}H_2 - CH = CH_2 \equiv \left[\overset{\delta-}{C}H_2 \cdots CH \cdots \overset{\delta-}{C}H_2\right]$

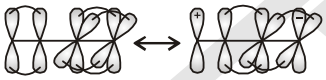
Eg. $CH_2 = CH - \overset{\oplus}{C}H_2$ 

$\overset{\oplus}{C}H_2 - CH = CH_2$ $\left[\overset{\delta+}{C}H_2 \cdots CH \cdots \overset{\delta+}{C}H_2\right]$

(4) $CH_2 = CH - \ddot{N}H_2 \longleftrightarrow \overset{\ominus}{C}H_2 - CH = \overset{\oplus}{N}H_2$

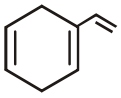
(5) $CH_2 = CH - \dot{C}H_2$ 

(6) $CH_2 = CH - BH_2$ 

(7) $CH_2 = CH - C \equiv CH \leftrightarrow \overset{\oplus}{C}H_2 - CH = C = \overset{\ominus}{C}H$ 

1. Resonance takes place due to delocalization of πe^-.

(a)  Resonance (b)  Resonance absent

(c)  Resonance (d)  Resonance

2. Position of the atoms remains the same, only delocalization of πe^- takes place.

Note:– $CH_3 - \overset{O}{\overset{\|}{C}} - NH_2 \longleftrightarrow CH_3 - \overset{OH}{\overset{|}{C}} = NH$ [They are not resonating structure rather they are **tautomer**]

3. Bond pair get converted into lone pair and l.p. get converted into b.p.

$\dot{C}H_3 = C - \ddot{N}H_2 \longleftrightarrow \overset{\ominus}{C}H_2 - C = \overset{\oplus}{N}H_2$

4. In Resonance No. of unpaired e^- remains the same

$CH_2 = CH - CH = CH_2 \longleftrightarrow \dot{C}H_2 - CH = CH - \dot{C}H_2$

(They are not resonating structure)

Resonating structure :

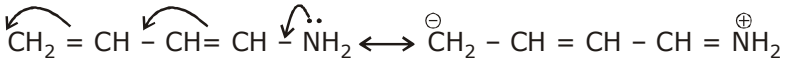
(1) Hypothetical strtucture exist on paper

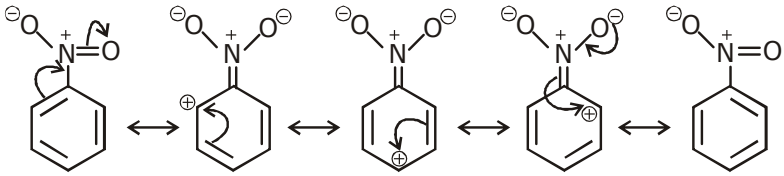
(2) The energy difference b/w different resonating structure is very small.

(3) All R. S. contribute twoards the formation of resonance hybrid (Their contribution may different)

(4) A single R. S. Can't explain each & every property of that particular compound

Draw the resonating structures : –

Q.1 

Q.2 
–m of NO_2 group

Resonance hybrid : –

It is a real structure which explain all the properties of a compound, formed by the contribution of different R. S.. It has got maximum stability as compared R. S.

Resonance Energy : –

It is the diffrence b/w theoretical value of H.O.H & experimental value.

Or

It is the difference b/w more stable R.S. & R. H.

* More the resonance energy, more stable will be the molecule.

* Cyclohexane is thermodynamically more stable than benzene, even though resonance energy of benzene is more.

* Resoance energy is a absolute term.

CONTRIBUTION OF DIFFERENT R. S. TOWARDS RESOANCE HYBRID

(1) Non-polar R. S. contribute more than polar R. S.

(a) $CH_2 = CH - CH = CH_2$ (b) $^{+}CH_2-CH = CH - CH_2^{\ominus}$ (c) $^{\ominus}CH_2 - CH = CH - CH_2^{+}$

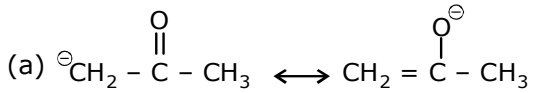
a > b = c stability

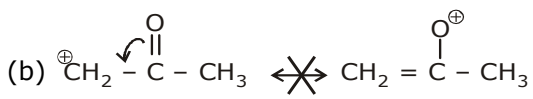
(2) Polar R. S. with complete octet will contribute more as compared with the one with incomplete octet

$CH_3 - CH^{+} - OCH_3 \longleftrightarrow CH_3 - CH = :O^{+} - CH_3$

Incomplete octet Complete octet

(3) In polar R. S. The –ve charge should be on more electro – ve atom & +ve charge should be on more electro + ve atom

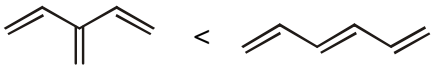
(a)  (more stable)

(b)  (less stable)

(4) Compound with more covalent bond will contribute more

(5) Unlike charges should be closer to each other whereas like charges should be isotated.

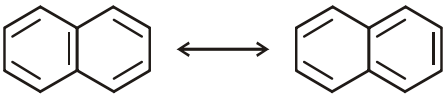
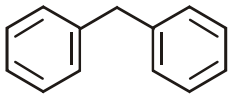
(6) Extended conjugation contribute more than cross conjugation.



Cross conjugation < Extended conjugation

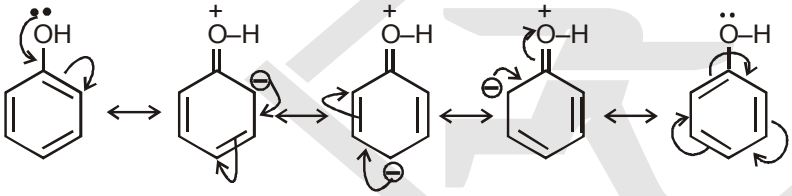
Fries Rule :–

Compound with more benzenoid structure are more stable as their Resonance energy is greater than those in which lesser no. of benzenoid structure are present.

R. E. is  < 

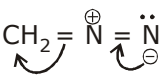
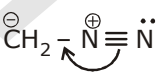
* If double bond is participating in resonance then it will aquire partial single bond character as a result of which bond length increase & bond strength decreases.
If a single bond is involved in resonance then it will aquire partial doulbe bond character. As a result of which bond length decreases & bond strength increase.

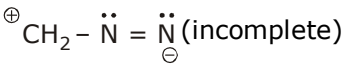
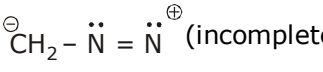
Q.1



(a) (b) (c) (d) (e)

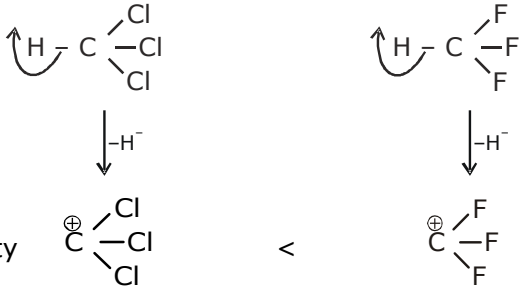
a = e > b = d > c

Q.2 (a)  (b) 

(c)  (incomplete) (d)  (incomplete)

a > b > c > d

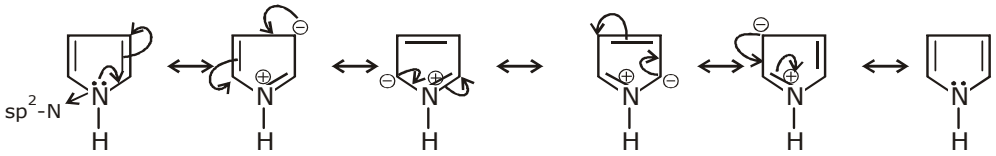
Q.3



Stability <

(back bonding)

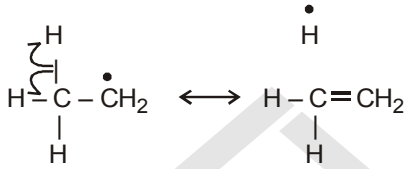
Q.4 (a) $\overset{\curvearrowleft}{CH_2} = CH \overset{\curvearrowleft}{F}$ (b) $^{\ominus}CH_2 - CH = F^+$ a > b (stability)

* 

Note:– When lone pair as well as double bond is present in some atom. Then only π bond will participating resonance. Where as lone pair remains sp^2 hybridised orbital.
When an atom has two or more then two lone pair then only one lone pair will participate in resonance and the other one remains in sp^2 hybridised orbital.

HYPER CONJUGATION

Permanent polarisation caused by displacement of σ-electrons into π-molecular orbital is known as hyperconjugation



Hyper conjugation is called No bond Resonance

* More α C – H bond, more will be the no bond resonating structure (Hyper conjugation)

• More α (C – H) bond, more will be the stability of free radical.

$$(CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3 - \dot{C}H_2 > \dot{C}H_3$$
$$9 \propto (C-H) \quad 6 \propto (C-H) \quad 3 \propto (C-H) \quad 0$$

Stability order

Properties of Free Radical

1. It is a neutral species.

2. It has one upaired electron that's why paramagnetic in nature.

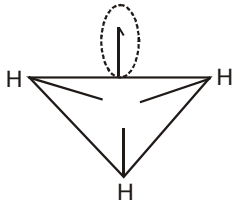
Structure :

$\dot{C}H_3$ → methyl free Radical

$\dot{C}H_3CH_2$ → ethyl free radical

3. its hydridisation is sp^2 and triangular planer shape.

Note : unpaired electron is not counted while calculating the hybridisation state.

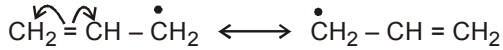


(unpaired electron stay perpendicular to the plane)

Stability of free Radical :

Its stability can be determined with the help of hyperconjugation as well as Resonance effect

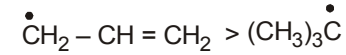
ALLYLIC FREE RADICAL



(Homolysis)

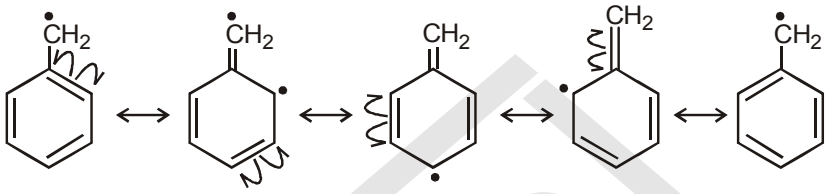
(Free Radical is on next carbon to doubly bonded carbon atoms)

Effect of Resonance > Hyper conjugation



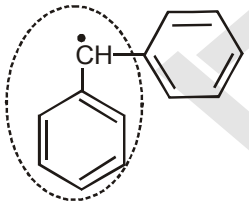
(stability)

BENZYLIC FREE RADICAL



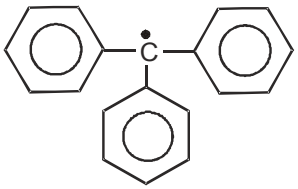
(4 Resonating structure)

* More Resonating structure, more will be the stability of the free Radical.



(di-benzylic free Radical)

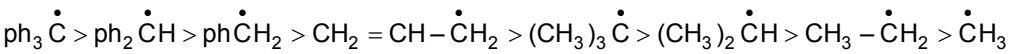
No. of Resonating structure = 7



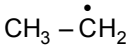
(Tri-benzylic free Radical)

No. of Resonating structure = 10

Stability Order :



Ex.1 Compare the stability of the following free Radical.

(a)  (b) (c)

Sol. (a) will be most stable due to hyper conjugation.

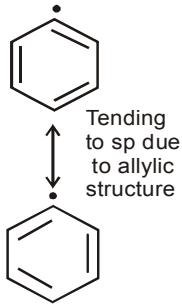
Between $CH_2 = \dot{C}H$ and $CH \equiv \underset{\downarrow}{\dot{C}}$ (sp)

$\Rightarrow$ more s-character
$\Rightarrow$ more electronegative
$\Rightarrow$ e^- density maximum
$\Rightarrow$ more repulsion
$\Rightarrow$ less stable

Ans. **a > b > c**

* More repulsion, less stability

Ex.2 Compare the stability of the following free Radicals

(a) 

(very unstable)

(b) $CH = \dot{C}H$ (sp^2)

(c) $CH \equiv \dot{C}$ actual sp
$\Rightarrow$ More repulsion
$\Rightarrow$ less stability

(Therefore this resonating structure is not possible)

Sol. **b > a > c**

Ex.3 (a) $CH_3 - \overset{*}{C}H(CH_3) - CH_3$ (b) $CH_3 - \overset{*}{C}H_2 - CH_3$ (c) $CH_3 - \overset{*}{C}H_3$ (d) $\overset{*}{C}H_4$

Compare the $\overset{*}{C}-H$ bond energy of the above compounds.

Sol. After forming free radical from the compound

$CH_3 - \dot{C}(CH_3) - CH_3$	$CH_3 - \dot{C}H - CH_3$	$CH_3 - \dot{C}H_2$	$\dot{C}H_3$
(3°)	(2°)	(1°)	methyl free radical
(a)	(b)	(c)	(d)

(most stable)
$\Downarrow$
therefore will have more
tendency to come in this form
$\Downarrow$
And C – H bond will break very readily

$\Rightarrow$ bond energies will be very less.

a < b < c < d < (bond energies order)

* $\text{Bond energy} \propto \frac{1}{\text{stability of free Radical}}$

* $\text{Bond length} \propto \text{stability of free Radical}$

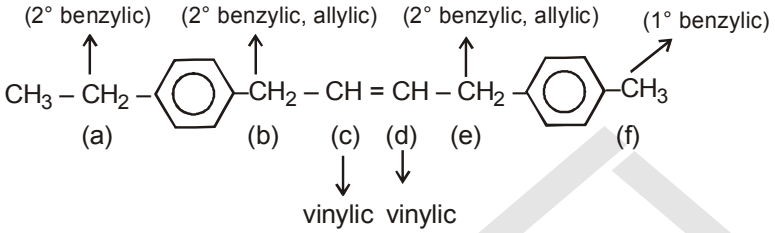
Ex.4 Compare the potential energy of the following compounds (above compounds)

Sol. If compound after being in free Radical form is very stable (i.e., less energy) it mean it would have possessed more energy initially i.e. it potential energy will be most

a < b < c < d

* Potential energy $\propto$ stability of free Radical

Ex.5 Compare the bond energies of C – H bond
(at a, b, c, d, e and f position)



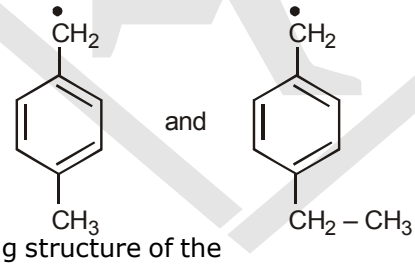
e > b > a > f > c = d

Stability order of free Radical that might be formed after removal of H (Homolytically) from the given carbon.

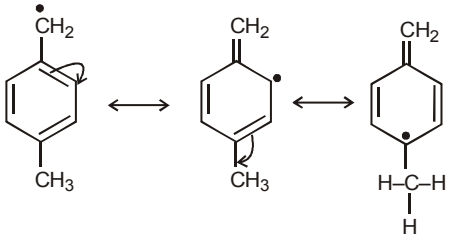
$\Rightarrow$ e < b < a < f < c = d

(C – H bond energies)

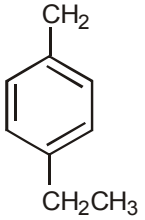
• In the above compound while comparing 2° benzylic allylic stability at two given position



while drawing the resonating structure of the

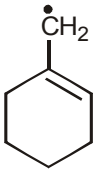


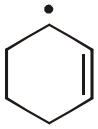
(Here inspite of Resonace three α (C – H) bond are available for no bond Resonance.

$\Rightarrow$ Therefore extra stable than  which have only two α (C – H) bond for Hyper conjugation.

Therefore 2° benzylic allylic corresponding to structure (a) is more stable than that of structure (b)

Ex.6 Compare the stability of the following free Radical


(a)

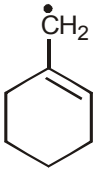

(b)

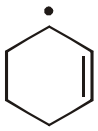

(c)

$CH_2 = CH - \dot{C}H_2$

(d)

Sol.


(a)


(b)


(c)

$CH_2 = CH - \dot{C}H_2$

(d)

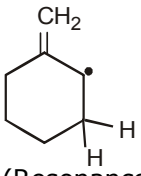
$\updownarrow$

$\dot{C}H_2 - CH = CH_2$ (only resonance)

(d)

1° allylic 2° allylic + 2αH 3° allylic + 5αH

$\updownarrow$



(Resonance + 2αH)

$\Rightarrow$ c > b > a > d

Ex.7 Compare the potential energy of $CH_3 - CH_3$, $CH_2 = CH_2$ $CH \equiv CH$

Sol. After making free Radical of the above compounds

$CH_3 - \dot{C}H_2$ (most – stable)' $CH_2 = \dot{C}H$ $CH \equiv \dot{C}$ (least stable)

$CH_3 - \dot{C}H_2 > CH_2 = \dot{C}H > CH \equiv \dot{C}$

(a) (b) (c)

a > b > c

CARBOCATION

$\overset{+}{C}H_3 \rightarrow$ Carbonium ion

$CH_3 - \overset{+}{C}H_2 \rightarrow$ Methyl carbonium ion

$CH_3 - CH(CH_3) - \overset{+}{C}H_2 \rightarrow$ Isopropyl carbonium ion

Properties of Carbocation :

1. it is positivly charged species
2. it has sixtet of electrons i.e. diamanetic
3. it is formed by heterolysis
4. it is generally formed due to polar solvent

Structure :

(sp^2) Triangular planer

Stability :

Its stability can be determined with the help of Inductive effect, Hyper conjugation and Resonance effect.

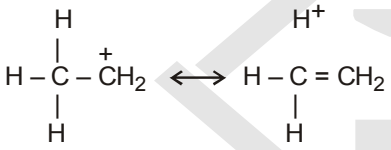
Stability of Carbocation :

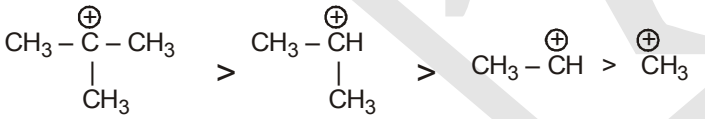
$\overset{+}{C}H_3$, $CH_3 \rightarrow \overset{+}{C}H_2$ (+ I effect)

$$\text{charge} \propto \frac{1}{\text{Stability}}$$

$\overset{+}{C}H_3$, < $CH_3 \rightarrow \overset{+}{C}H_2$ (stability order)

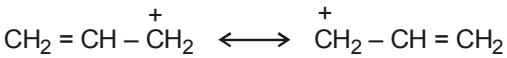
Stability of carbocation can also be determined by Hyper conjugation (no bond Resonance)





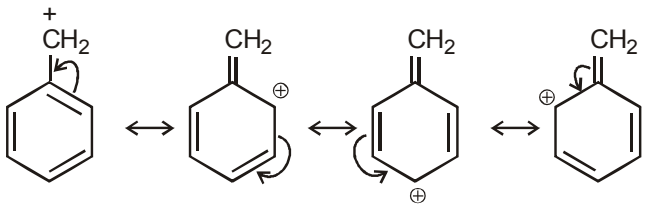
9α C – H bond 6α C – H bond 3α C – H bond

ALLYLIC CARBOCATION



allylic carbocation Actual Resonance

BENZYLIC CARBOCATION



$ph_2\overset{+}{C}H \rightarrow$ 7 Resonating strucutre

$ph_3\overset{+}{C} \rightarrow$ 10 Resonating strucutre

$ph_3\overset{+}{C} > ph_2\overset{+}{C}H > (CH_3)_3\overset{+}{C} > ph\overset{+}{C}H_2$

Ex.8 Compare the stability of th following carbocation

(a) $CH_3-\overset{+}{C}H_2$ (b) $CH_2=\underset{\downarrow}{\overset{+}{C}H}$ (sp^2) (c) $CH\equiv\underset{\downarrow}{\overset{+}{C}}$ (sp)

$\Rightarrow$ more s charactor

$\Rightarrow$ more electronegativity

$\Rightarrow$ +ve charge on more electronegative element is symbol of unstability.

a > b > c

Ex.9 Compare the stability of the following compounds

(a) $\overset{+}{C}H_2-CF_3$ (b) $\overset{+}{C}H_2-CCl_3$ (c) $\overset{+}{C}H_2-CBr_3$ (d) $\overset{+}{C}H_3$

Sol. d > c > b > a

F being most electron attracting group decreases the e^- density from positively charged C-atom and decreases the charge density and makes the carbocation less stable.

Ex.10 Compare the stability of the following carbocation :

(a) $\overset{+}{C}H_2-F$ (b) $\overset{+}{C}H_2-Cl$ (c) $\overset{+}{C}H_2$–Br (d) $\overset{+}{C}H_2-I$

Sol. due to greater size of Iodine, its L.P. will not be available for coordinate bond. Therefore L.P. would not stabilize corbocation.

In case of F due to its small size its lone pair can be easily coordinated to $\overset{\oplus}{C}$ making it most stable

a > b > c > d (Stability)

* By coordination the carbocation completes its octet and structure having complete octet of its atom is supposed to be most stable.

$\overset{\oplus}{C}H_2-\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}: \leftarrow\rightarrow \overset{\oplus}{C}H_2 \leftarrow F \cong CH_2=\overset{\oplus}{F}$

(Each atom has its full octet)

* $>\overset{\oplus}{C}-\ddot{A} > ph_3\overset{\oplus}{C}$

(stability)

Note : In Rasonating Structure of $ph_3\overset{+}{C}$, at least one C gets sixtet of e^- and hence less stable than coordinated compound.

Ex.11 Compare the stabilities of the following corbocation

(a) $\overset{+}{C}H_2NH_2$ (b) $\overset{+}{C}H_2-OH$ (c) $\overset{+}{C}H_2-F$

Sol. N, O, F belongs to same period

$\Rightarrow$ In period Electronegativity of the atom is deciding factor

$\Rightarrow$ F being most electronegative, holds its e^- pair very firmly.

$\Rightarrow$ Its L.P. will not be easily available for coordination.

$\Rightarrow$ Stability by it will be minimum.

a > b > c

Ex.12 Compare the following corbocation in order of their stability.

(a) $\overset{+}{C}H_2 - Cl$ (b) $\overset{+}{C}H_2 - OH$

Sol. If periods of atoms which have to donate their electrons for coordination (for stability) is different then atomic size will be deciding factor. The atom whose size is greater will be unable to make its e^- pair available for coordination.

b > a

Ex.13 Compare the stability of the following compounds

(a) $CH_3 \rightarrow CH_2 - \overset{+}{C}H_2$ (b) $CH_2 = CH - \overset{+}{C}H_2$ (allylic) (c) $ph \leftarrow CH_2 - \overset{+}{C}H_2$

Sol $\Rightarrow$ more s-character

$\Rightarrow$ more e.n.

$\Rightarrow$ attracts e^-

$\Rightarrow$ reduces, stability

b > a > c

CARBANION

1. it is a –ve charged species **2.** it has octet of electrons. **3.** diamagnetic

Strucutre :

***** if –ve charge is in Resonance then the hybridisation of carbanion is sp^2 (Triangular planer shape)

* If –ve charge is not in Resonance then the hybridisation of carbanion is sp^3 (pyramidal)

Stability :

Its stability can be determined with the help of

(1) Inductive effect

(2) Resonance effect

Ex.14 $\overset{\ominus}{C}H_3$, $CH_3\overset{\ominus}{C}H_2$

(a) (b)

a > b (stability)

* Stability of the carbanion is as follows

$$ph_3\overset{\ominus}{C} > ph_2\overset{\ominus}{C}H > ph\,\overset{\ominus}{C}H_2 > CH_2 = CH - \overset{-}{C}H_2 > CH \equiv \overset{-}{C} > CH_2 = \overset{-}{C}H > \overset{-}{C}H_3 > CH_3 - \overset{\ominus}{C}H_2 > (CH_3)_2\overset{-}{C}H > (CH_3)_3\overset{-}{C}$$

Ex.15 Compare the stability of the following carbacation

(a)  (b) $CH \equiv \overset{+}{C}$ actual(sp) (c) $CH_2 = \overset{+}{C}H$ sp^2

tending to sp

Sol. **c > a > b**

Ex.16 Compare the stability of the following carbanion

(a)  tending sp (b) $CH \equiv \overset{\ominus}{C}$ sp –ve charge is attracted by sp hybridised carbon (most electronegative) ⇒ become more stable (c) $CH_2 = \overset{\ominus}{C}H$ sp^2

Sol. **b > a > c**

Ex.17 Compare the stability of the following carbanion

(a) $\overset{\ominus}{C}H_2 - CF_3$ (b) $\overset{\ominus}{C}H_2 - CCl_3$ (c) $\overset{\ominus}{C}H_2 - CBr_3$

Sol. a > b > c

Ex.18 Arrange the following anion order of their stability

(a) Cl^-, (b) Br^- (c) F^- (d) I^- (maximum size)

⇒ maximum dispersion of –ve charge

⇒ max stability

Sol. d > b > a > c

Ex.19 Compare the stability of the following

(a) $\overset{\ominus}{C}H_3$ (b) $\overset{\ominus}{N}H_2$ (c) $\overset{\ominus}{O}H$ (d) $\overset{\ominus}{F}$

Sol. Same period element (C, N, O, F)

⇒ Stability ∝ E.N. of the atom

d > c > b > a

Ex.20 Compare the acidic strength

(a) HCl (b) HF (C) HBr (D) HI

Sol. Acidic strength ∝ stability of the anion formed (conjugate base)

as we know $I^- > Br^- > Cl^- > F^-$

⇒ H I > HBr > HCl > HF

Ex.21 Compare the Acidic strength of the following

(a) NH_3 (b) pH_3 (c) AsH_3 (d) SbH_3 (e) BiH_3

Sol. Anion formed from there acids are

$\bar{N}H_2 < \bar{P}H_2 < \bar{A}sH_2 < \bar{S}bH_2 < \bar{B}iH_2$

(Stability)

$\Rightarrow$ acidic strength e > d > c > b > a

Ex.22 Compare the acidic strength of the following comounds

CH_4, NH_3, H_2O, HF

Sol. The conjugate base of the given acid is as follows

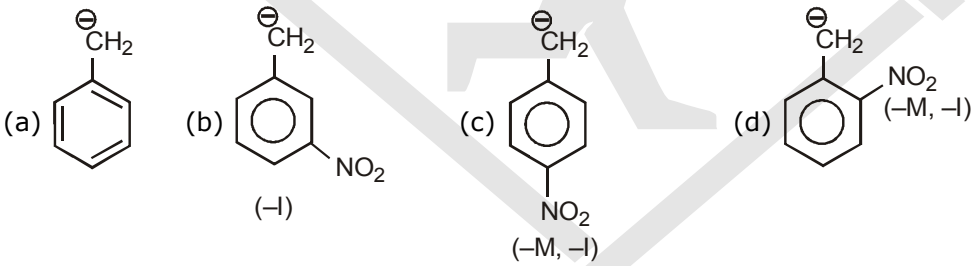
$\overset{\ominus}{C}H_3, \overset{\ominus}{N}H_2, \overset{\ominus}{O}H, \overset{\ominus}{F}$

we have already proved that

$\overset{\ominus}{F} > \overset{\ominus}{O}H > \overset{\ominus}{N}H_2 > \overset{\ominus}{C}H_3$ (Stability)

$\Rightarrow$ $HF > H_2O > NH_3 > CH_4$ (acidic strength)

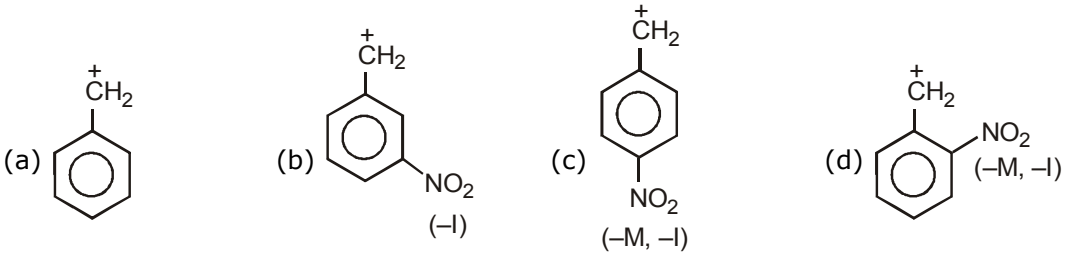
Ex.24 Compare the stability of the following carbanion.



Sol. d > c > b > a

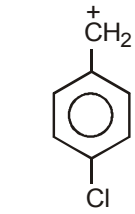
* +M or –M is not distance dependent

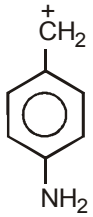
Ex.25 compare the stability of the following carbocation

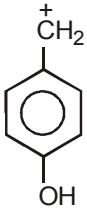


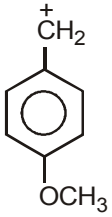
Sol. **a > b > c > d**

Ex.26 Compare the stability of the following carbocation.

(a) 
(+M, –I)
but –I > +M for Cl

(b) 
(+M)

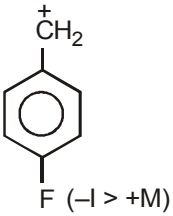
(c) 
(+M)

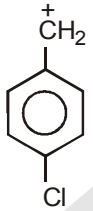
(d) 
(+M)

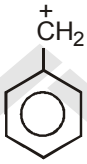
Sol. +M (OH) > +M (OCH_3)

b > c > d > a

Ex.27 Compare the stability of the following carbocation

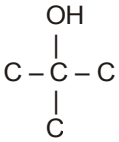
(a) 

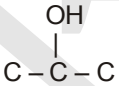
(b) 

(c) 

Sol. c > a > b

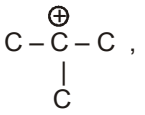
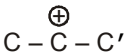
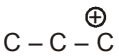
Ex.28 Compare order of dehydration of the following alcohols :

(a) 

(b) 

(c) C – C – C – OH

Sol. After formation of carbocation

 ,  

Since 3° carbocation is most stable therefore it will show greatest tendency to lose water as after lose of water it comes in stable form.

TYPES OF REAGENT

1. **Electrophilic reagent** : All electron deficient atom or group of atoms is known as Electrophilic reagent, the electrophile attacks at the electron rich centre.

(a) all positively charged species are electrophile

H^+, NO_2^+, Br^+, Cl^+, etc.

(b) The compound in which the octet of central atom is not complete

BF_3, $AlCl_3$, $ZnCl_2$, etc.

(c) all the compound in which the central atom can expand its octet

$SnCl_4$, $SiCl_4$, etc.

(d) all polarising functional group are electrophile as well as nuelophile

$>C=O$, $-C\equiv N$, etc.

Nucleophile :

All electron rich compounds are nucleophile and attack at the electron deficient centre.

(a) all negatively charqed species

H^-, Cl^-, NO_2^-, Br^-, CH_3^- etc.

(b) the compound in which the central atom has lone pair of electron.

NH_3, H_2O, $R\ddot{N}H_2$, $R\ddot{O}H$ etc.

(c) all organometallic compounds are nucleophile

R – Mgx, RLi, R_2Cd

(d) The compound having π e^- density, $CH_2=CH_2$,  etc.

Nucleophilicity :

The power of nucleophile is known as nucleophilicity .

$\Rightarrow$ The nucleophilicity of negative charge is greater than the nucleophilicity of lone pair

$\bar{O}H > H_2O$

$CH_3\bar{O} > CH_3OH$

$\Rightarrow$ If lone pair or –ve charge is present on the different atom then less electronegativity, more will be the nucleophilicity.

CH_3^-, NH_2^-, OH^-, F^-

Nucleophilicity $CH_3^- > NH_2^- > OH^- > F^-$

$\Rightarrow$ $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$ (Nucleophilicity)

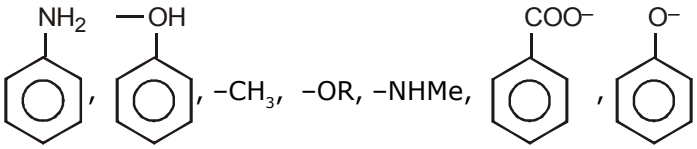
$\Rightarrow$ If –ve charge or lone pair of electron is present on the same atom then the less stable –ve charge will be the better nucleophile

$OH^-, CH_3\bar{O}, CH_3COO^-$

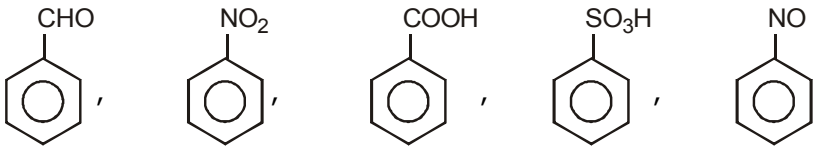
$CH_3O^- > OH^- > CH_3COO^-$ (nucleophilicity)

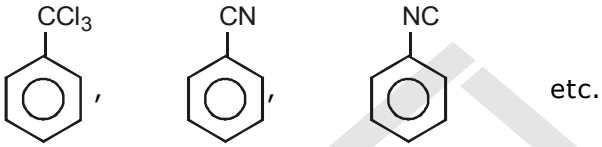
ACTIVATOR & DEACTIVATOR

The groups in benzene which show +M effect or +I effect Increases the electron density on benzene it means they activate the ring towards electrophile and known as activator.



The groups which shows –M or –I effect (resultant) decreases the e^- density from benzene ring. It means they deactivate the ring towards electrophile

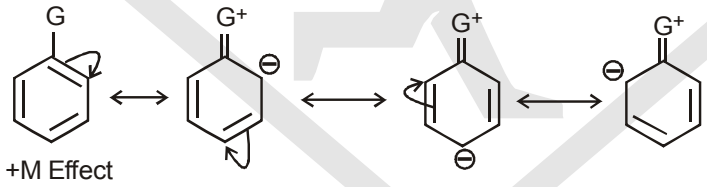




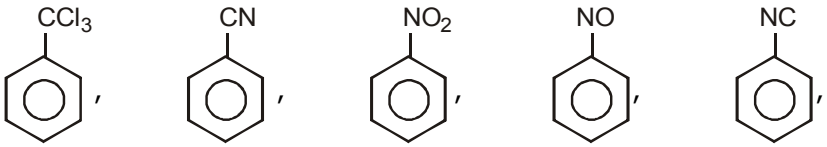
etc.

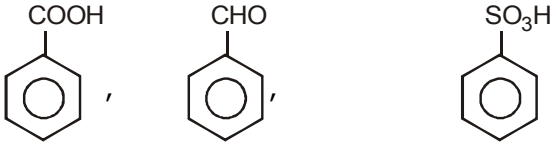
ORTHO, PARA & META DIRECTOR

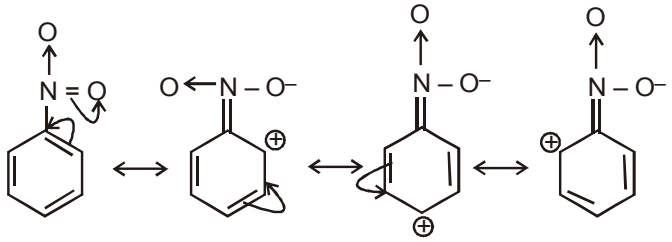
The groups which shows +I (resultant) or +M effect then negative charge is developed at the ortho & para position. Therefore electrophile attack at the ortho & para position and the groups are known as OP director.



- The groups which shows –M effect or – I effect (resultant) then +ve charge is developed at the ortho & para position this means electron density is minimum at the ortho & para positions and electronphile will attack at the meta position the groups are known as meta director.







HEAT OF HYDROGENATION(H.O.H)

It is the amount of energy realeased when one mole of H_2 is added to any unsaturated system.

$$CH_2 = CH_2 + H_2 \rightarrow CH_3 - CH_3 + \text{energy}$$

HOH is exothermic process $\Delta H = -$ ve

*HOH $\propto$ No. of π-bonds in compound

If no. of π-bonds is same then

$$*HOH \propto \frac{1}{\text{stability of compound}}$$

$\therefore$ In case of alkene

$$**HOH\ \alpha\ \frac{1}{\text{stability of compound}}\ \alpha\ \frac{1}{\text{No. of } \alpha H}$$

Ex.

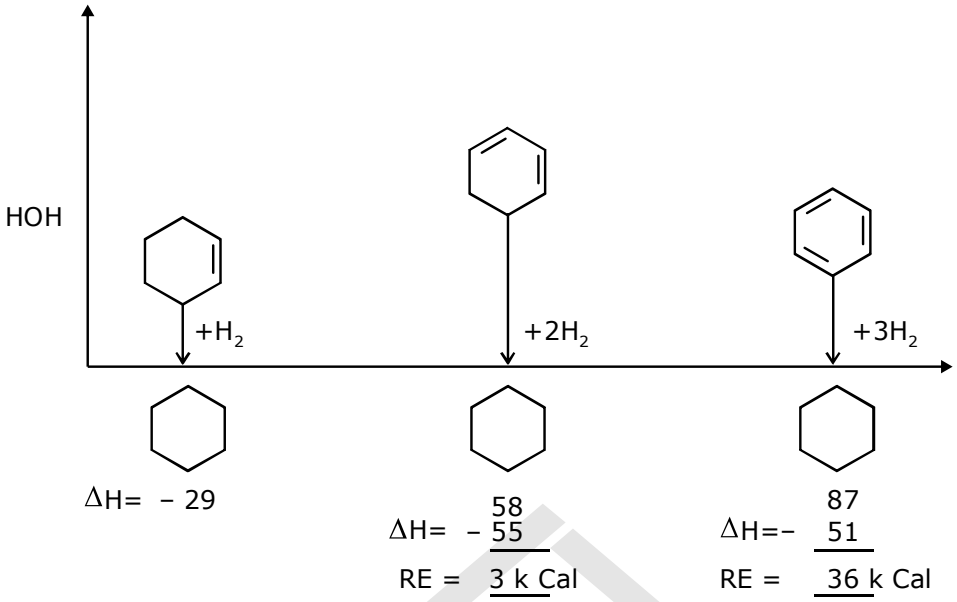
a  + H_2 ⟶  + 29 kcal

b  + 2 H_2 ⟶  + 58 kcal (expected) ⟹ 55 kcal (actual)

c  + 3 H_2 ⟶  + 87 k cal (expected) ⟹ 51 k cal (actual)

b > c > a

Energy



Some examples of Arromatic(A), Non-arromatic(NA) and Anti-arromatic(AA)

(1)  (A)

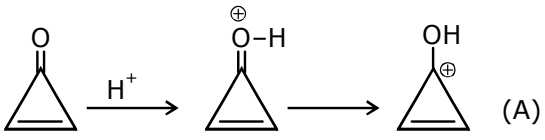
(2)  (AA)

(3)  (AA)

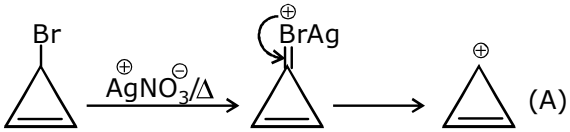
(4)  (NA)

(5)  (AA)

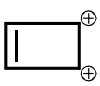
(6)  (A)

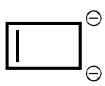
(7) 

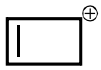
(A)

(8) 

(A)

(9)  (A) (2πe)

(10)  (A) (6πe)

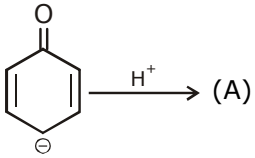
(11)  (NA)

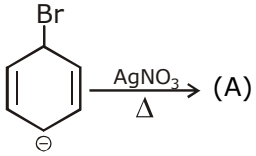
(12)  (NA)

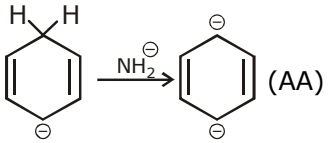
(13)  (AA) (4πe)

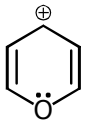
(14)  (A)

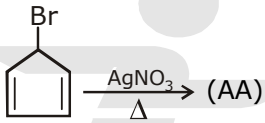
(15)  (NA)

(16) 

(17) 

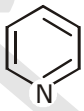
(18) 

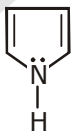
(19)  (A)

(20)  (AA)

(21) 

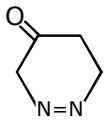
(22)  (AA)

(23)  (A)

(24)  (A)

(25)  (A)

(26)  (A)

(27)  (NA)

Acidity & Basicity

$HA \rightleftharpoons H^{\oplus} + \overset{\ominus}{\ddot{A}}$

Acid Conjugate base

Note : More stable the conjugate base (i.e., $\overset{\ominus}{\ddot{A}}$), more will be the forward reaction which results more acidic nature of HA.

Ex.1 Compare the acidic strength of the following acids.

(a) C – C – C – COOH (b) C = C – C – COOH (c) C ≡ C – C – COOH

Sol. The acid whose conjugate base is most stable will be more acidic.

After forming conjugate base from the above acids.

(a) C – C – C – COO$^{\ominus}$ (sp^3) (b) C = C – C – COO$^{\ominus}$ (sp^2) (c) C ≡ C – C – COO$^{\ominus}$ (sp)

It is clear that sp hybridised carbon being most electronegative will decrease e^- density from O most effectively making the conjugate base most stable.

c > b > a (acidic strength)

Ex.2 Which is more acidic between the two

(a) CHF_3 (b) $CHCl_3$

Sol. $CHF_3 > CHCl_3$

If we consider the –I effect of F and Cl But this effect will not be considered here

After the removal of proton

(a) $\ominus CF_2F$ (b) $\ominus CCl_2Cl$

(vacant d-orbital available where C will coordinate its electron) ($p\pi - d\pi$ bonding)

$\Rightarrow$ a < b (acidic strength)

Ex.3 Compare the acidic strength of the following

(a) CHF_3 (b) $CHCl_3$

(c) $CHBr_3$ ($p\pi - d\pi$ bonding in Br is not as much as effective as in Cl due to large size of Br)

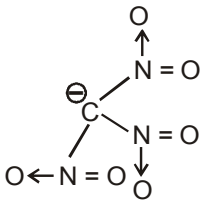
Sol. $CHCl_3 > CHBr_3 > CHF_3$

Ex.4 Compare the acidic strength of the following

(a) $CH(CN)_3$ (b) $CH(NO_2)_3$ (c) $CHCl_3$

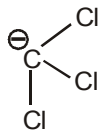
Sol. After removing H^+

$^-C(C\equiv N)_2(C\equiv N)$ (Resonance) In its resonating structure, –ve charge will be on N)



(Resonance) (– In its resonating structure –ve charge will reside on O

⇒ more effective Resonance



($p\pi - d\pi$)

b > a > c

* –ve charge on O is more stable than –ve charge on N as O is more electronegative than N.

* $P\pi - d\pi$ Resonance < Actual Resonance

Ex.5 Compare the acidic strength of the following

(a) $CH \equiv CH$ (b) $CH_2 = CH_2$ (c) $CH_3 - CH_3$

Sol. $\underset{sp}{CH \equiv \bar{C}} > \underset{sp^2}{CH_2 = \bar{C}H} > \underset{sp^3}{CH_3 - \overset{\ominus}{C}H_2}$

(Stability of the conjugate base)

⇒ a > b > c (acidic strength)

Ex.6 Compare the acidic strength of the following :

(a) $CH_3 - CH_2 - CH_2 - COOH$

(b) $CH_3 - CH_2 - \underset{\displaystyle Cl}{\underset{|}{CH}} - COOH$

(c) $CH_3 - CH_2 - \underset{\displaystyle F}{\underset{|}{CH}} - COOH$

(d) $CH_3 - CH_2 - \underset{\displaystyle NO_2}{\underset{|}{CH}} - COOH$

Sol. **d > c > b > a**

Ex.7 Compare the acidic strength of the following :

(a) H_2O (b) H_2S (c) H_2Se (d) H_2Te

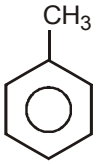
Sol. Conjugate base is in an stability order

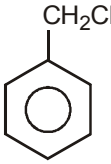
$\bar{O}H < H\bar{S} < H\bar{S}e < H_2Te$

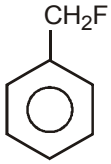
$\Rightarrow$ $H_2O < H_2S < H_2Se < H_2Te$ (acidic strength)

Ex.8 Compare the acidic strength of the following compound

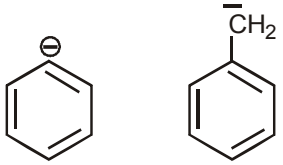
(a) 

(b) 

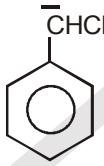
(c) 

(d) 

Sol. After forming conjugate base of the above

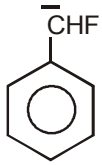


–ve charge is not in resonance



pπ – dπ bonding due vacant d-orbital of Cl

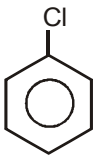
(most stable)

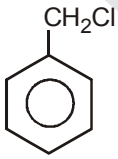


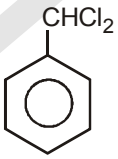
C – I effect of F decrease e^- density from C making the carbanion stable

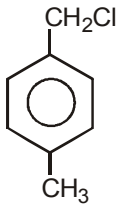
c > d > b > a

Ex.9 Compare the reactivity of the following compounds with 1 mole of $AgNO_3$

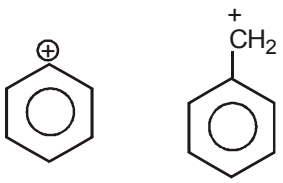
(a) 

(b) 

(c) 

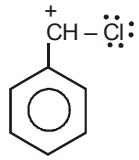
(d) 

Sol. After removing Cl^-

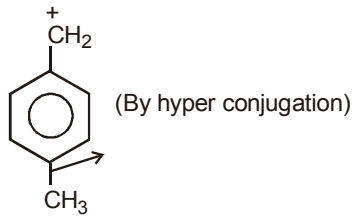


(+ve charge is not on resonance

$\therefore$ least stable)



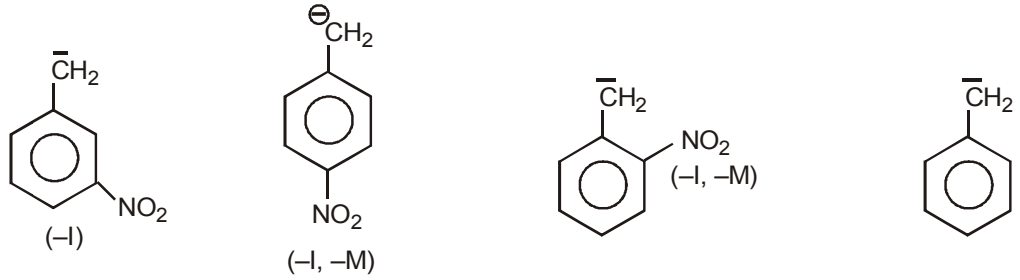
(most stable as L.P. of Cl will be coordinated to +ve charge completing the octet of each atom and making the corbocation most stable)



extent of +ve charge decreases stability increases

Ex.10 Compare the acidic strength

Sol. After making conjugate base



c > b > a > d

BASIC STRENGTH

$A^+ - H$

Basic strength directly depends on the availibility of lone pair for H^+

Ex.11 Compare the basic strength of following

Sol.

(a) NH_3 ↑
(b) PH_3
(c) AsH_3 — Basic strength
(d) SbH_3
(e) BiH_3

Ex.12 Compare the basic strength of the following

(a) $\bar{C}H_3$ (b) $\bar{N}H_2$ (c) $\bar{O}H$ (d) $\bar{F}$

Sol. $\bar{C}H_3$, $\bar{N}H_2$, $\bar{O}H$, $\bar{F}$

$CH_4 < NH_3 < H_2O < HF$

(acidic strength)

$\overset{\ominus}{C}H_3 > \overset{\ominus}{N}H_2 > \bar{O}H > \bar{F}$

(Basic strength)

* Strong Acids have weak conjugate base.

$\overset{\ominus}{C}H_3 > \overset{\ominus}{N}H_2 > \bar{O}H > F$

(Nucleophilicity)

* For the same period
less electronegativity, more nucleophilicity as more electronegative element has less tendencey to give its electron pair.

Ex.13 Which is more basic $\bar{O}H$ or $H\bar{S}$?

Sol. $\bar{O}H > H\bar{S}$

Which is more basic NH_3 or $\overset{\ominus}{N}H_2$

forming conjugate acid

$\overset{+}{N}H_4 > NH_3$ (acidity)

$\therefore$ $NH_3 < \overset{\ominus}{N}H_2$ (Basicity)

COMPARISON OF BASICITY OF AMMONIA AND ALKYL AMINES :

Ex.14 Compare the basic strength of the following NH_3, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$

Factors which affect the basicity of Amines

(1) steric effects

(2) Inductive effect

(3) solvation effect.

- The base whose conjugate acid is more stable will be more acidic forming conjugate acid of the given base

$\overset{+}{N}H_4$, $CH_3\overset{+}{N}H_3$, $(CH_3)_2\overset{+}{N}H_2$, $(CH_3)_3\overset{+}{N}H$

Stability order of conjugate acid

$(CH_3)_3\overset{+}{N}H > (CH_3)_2\overset{+}{N}H_2 > CH_3\overset{+}{N}H_3 > \overset{+}{N}H_4$

(due to +I effect)

Therefore basic strength

$(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$

(vapor phase or gaseous is phase or in Non polar solvent)

In Aqueous solution or in polar solvent

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

- In aqueous solution, the conjugate acids form H-bonds (intermolecular) with water molecules and stabilise them selves conjugat acid of 1° amine which has largest no. of H-atoms form maximum H-bond with water and is most stable. Consequently 1° amine is most basic.

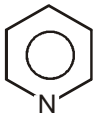
- Due to steric effect 1° amine is considered more basic as compared to 3° amine as lone pair is hindered by three alkyl group and less available for H^+.

  Considering the combined effect of the three (Inductive, solvation and steric effect) we can conclude that

  $2° > 1° > 3° > NH_3$

- Aromatic amines are least basic as their lone pair is in conjugation and less avaibable for protonation.

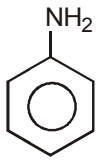
Ex.15 Compare the basic strength of the following

(a) 

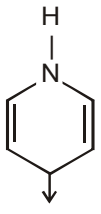
(no Resonance as ring will break if we draw the resonating structure)

⇓

(most basic)

(b) 

(Resonance)

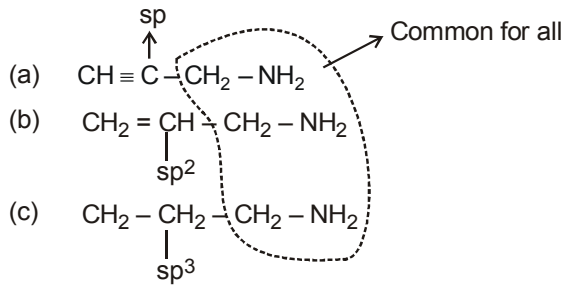
(c) 

(if L.P. will be participate in Resonance, then molecule becomes aromatic)

$\therefore$ Hence L.P. will have a greater tendency to take part in Resonance and will be less available for H^+

$\therefore$ This compound will be least basic.

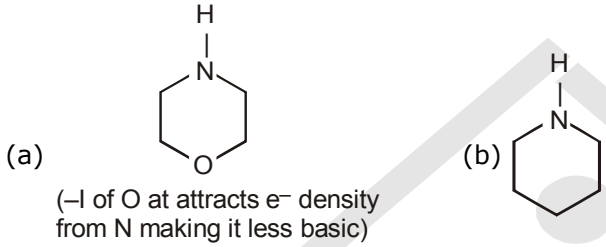
Ex.16 Compare the basic strength of the following



Sol. sp hybridised carbon being most electronegative will attract e^- density from nitrogen and will make it less available for H^+. Hence basicity decreases.

c > b > a

Ex.17 Compare the basic strength



a < b

Ex.18 Compare the basicity of the following compounds

(a) $CH_3 - CH_2 - CH = CH - \ddot{N}H_2$

(b) $CH_3 - CH_2 - \underset{\downarrow}{CH_2}{}^{sp^3} - CH_2 - NH_2$

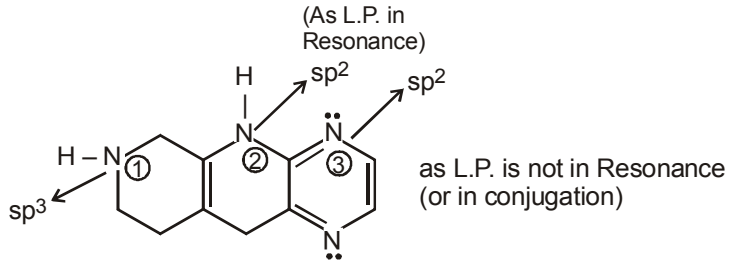
(c) $CH_2 = CH - \underset{\downarrow}{CH_2}{}^{sp^2} - CH_2 - NH_2$

(d) $CH \equiv \underset{\downarrow}{C}{}^{sp} - CH_2 - CH_2 - NH_2$

Sol. In part (a) the lone pair of nitrogen in Resonance therefore will be less available for H^+ making it least basic among all followed by sp, sp^2, sp^3 hybridised carbon atoms.

b > c > d > a

Ex.19 Compare the basicity of the numbered nitrogen atoms.



Sol. The planerity of ring will be destroyed if L.P. will take part in Resonance.

Basicity order of Nitrogen follows the order

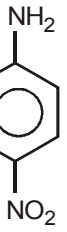
$N(sp^3) > N(sp^2) > N(sp)$

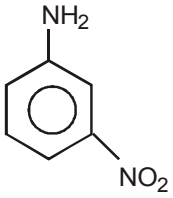
1 > 3 > 2

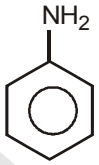
sp^2 sp^2

(In this sp^2, l.p. is in Resonance with ring hence will be less available for H^+ therefore it will be least basic)

Ex.20 Compare the basic strength of the following

(a) 

(b) 

(c) 

Sol. In part (a) NO_2 is at p-position Hence will attract e^- density by both –M and –I

In part (b) NO_2 is at m-position hence will attract e^- density by –I only

There is no such effect in part (c)

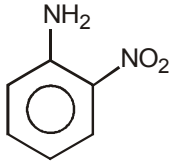
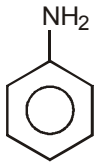
⇒ Availibity of L.P. on nitrogen in part (a) is minimum followed by b and then c.

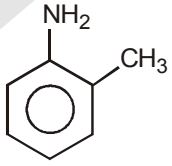
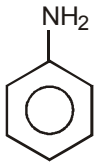
c > b > a

Ortho effect :

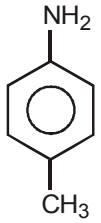
The ortho substituted aniline are less basic than aniline and ortho substituted benzoic acids are more acidic than benzoic acid.

- Ortho effect is valid only for benzoic acid and aniline.

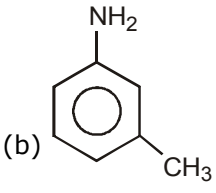
e.g.  < 

Also  < 

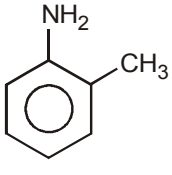
Ex.21 Compare the basic strength of the following :

(a) 

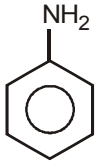
(+I, Hyperconjugation)

(b) 

(+I)

(c) 

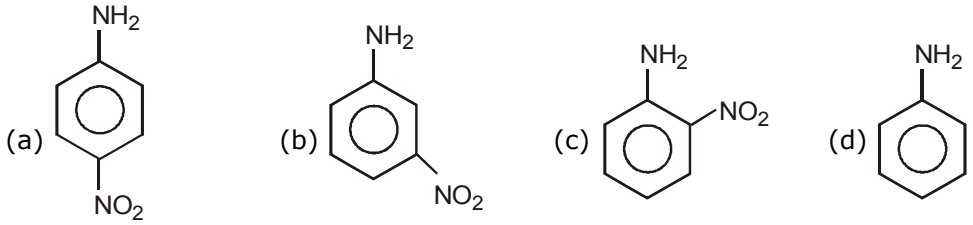
(+I)

(d) 

Sol. **a > b > d > c**

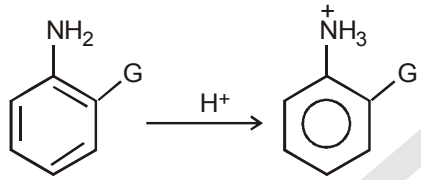
* Due to ortho effect d > c
if c is less basic than d then it will be certainly less basic than b as b is more basic than d.

Ex.22 Compare the basic strength of the following :



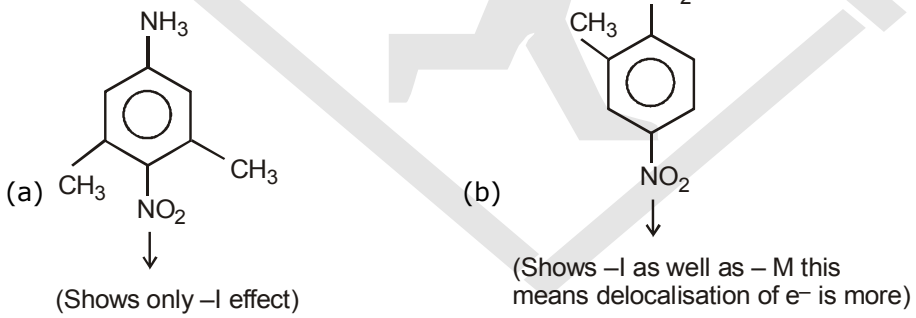
Sol. Do your selves

S.I.P → Steric inhibition of Protonation (ortho effect)



after protonation, repulsion increases therefore ortho substituted aniline is less basic than aniline

S.I.R → Steric inhibition of resonance



EXERCISE – I

JEE MAIN

1. Bond formation is:

   (A) always exothermic

   (B) always endothermic

   (C) neither exothermic nor endothermic

   (D) sometimes exothermic and sometimes endothermic

Sol.

2. $CH_2 = CH - CN$

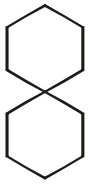
   3 2 1

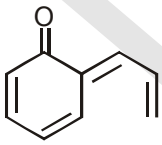
   C1 - C2 bond of this molecules is formed by:

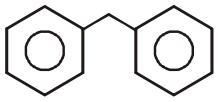
   (A) sp^3-sp^2 overlap (B) sp^2-sp^3 overlap
   (C) sp^2-sp overlap (D) sp^2-sp^2 overlap

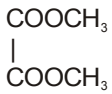
Sol.

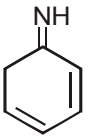
3. In which of the following molecules resonance takes place through out the entire system

(A) 

(B) 

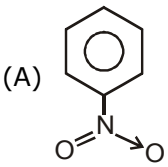
(C) 

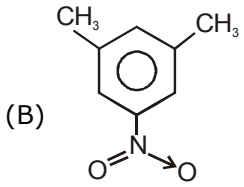
(D) 

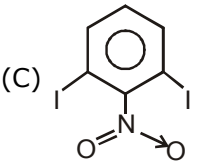
(E) 

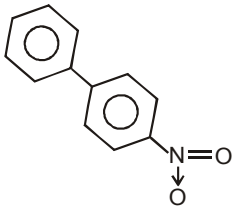
Sol.

4. In which of the following molecules – NO_2 group is not coplanar with phenyl ring ?

(A) 

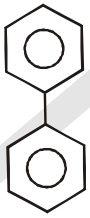
(B) 

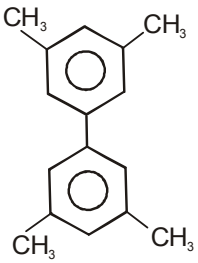
(C) 

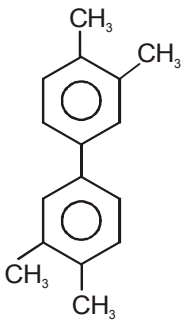
(D) 

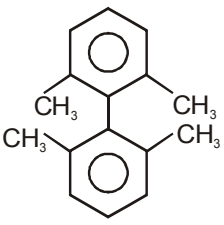
Sol.

5. In which of the following molecels both phenyl rings are not coplanar ?

(A) 

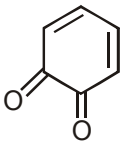
(B) 

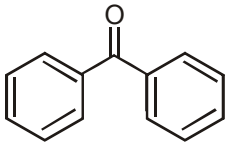
(C) 

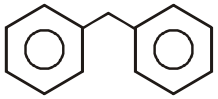
(D) 

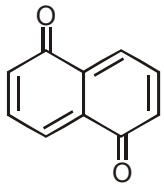
Sol.

6. In which of the following molecules, all atoms are not coplanar ?

(A) 

(B) 

(C) 

(D) 

Sol.

7. (I) $CH_3 - CH = O$ (II) $CH_2 = CH - OH$

(II) $CH_3 - \overset{\oplus}{C}H - \overset{\ominus}{O}$

Among, these, which are canonical structures ?

(A) I and II (B) I and III

(C) II and III (D) all

Sol.

8. (I) $CH_2 = CH - CH = CH_2$

(II) $\overset{\ominus}{C}H_2 - CH = CH - \overset{\oplus}{C}H_2$

(II) $\overset{\oplus}{C}H_2 - CH = CH - \overset{\ominus}{C}H_2$

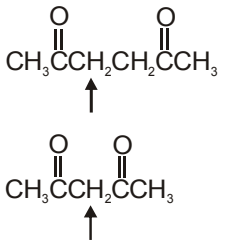
Among, these, which are canonical structures ?

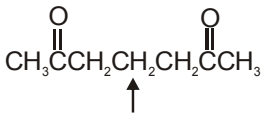
(A) I and II (B) I and III

(C) II and III (D) all

Sol.

9. Rank the following compounds in order of decreasing acidity of the indicated hydrogen :

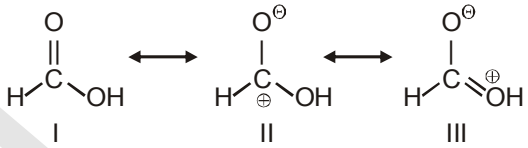




(A) I > II > III (B) III > I > II

(C) I > III > II (D) III > II > I

Sol.

10. 

Among these canonical structures, the correct order of stability is

(A) I > II > III (B) III > II > I

(C) I > III > II (D) II > I > III

Sol.

11. (I) $CH_2 = CH - CH = CH - OCH_3$

(II) $\overset{\ominus}{C}H_2 - CH = CH - CH = \overset{\oplus}{O}CH_3$

(III) $CH_2 = CH - \overset{\ominus}{C}H - \overset{\oplus}{C}H - OCH_3$

(IV) $CH_2 = CH - \overset{\oplus}{C}H - \overset{\ominus}{C}H - OCH_3$

Amongt these canonical structures which one is least stable ?

(A) I (B) II

(C) III (D) IV

Sol.

12. $CH_2 = CH - CH = CH - CH_3$ is more stable than $CH_3 - CH = C = CH - CH_3$ because

(A) there is resonance in I but not in II

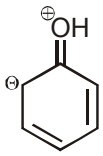
(B) there is tautomerism in I but not in II

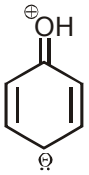
(C) there is hyperconjugation in I but not in II

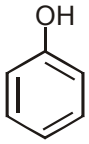
(D) II has more cononical structures than I.

Sol.

13. For phenol which ofthe following resonating structure is the most stable ?

(A) 

(B) 

(C) 

(D) All haveequal stability

Sol.

14. (I) $CH_3 - O - CH = CH - CH = CH_2$

(II) $CH_3 - O - \overset{\oplus}{C}H - CH = CH - \overset{\ominus}{C}H_2$

(III) $CH_3 - \overset{\oplus}{O} = CH - CH = CH - \overset{\ominus}{C}H_2$

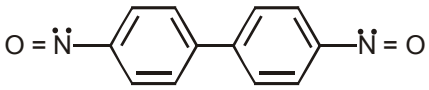
Among these three canonical structures (through more are possible) what would be their relative contribution in the hybrid

(A) I > II > III (B) III > II > I

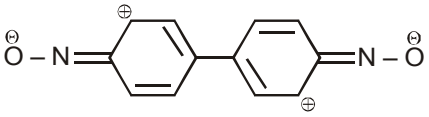
(C) I > III > II (D) III > I > II

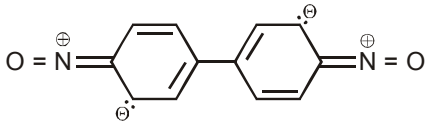
Sol.

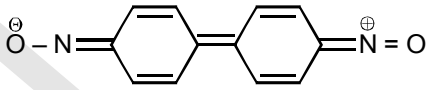
15. The most stable resonating structure of following compound is



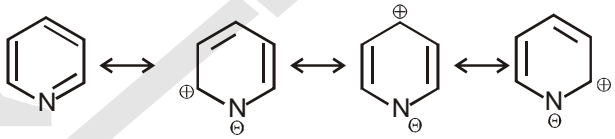
(A) 

(B) 

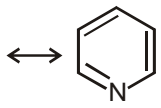
(C) 

(D) 

Sol.

16. 

I II III IV



V

Among these canonical structures of pyridiine, the correct order of stability is

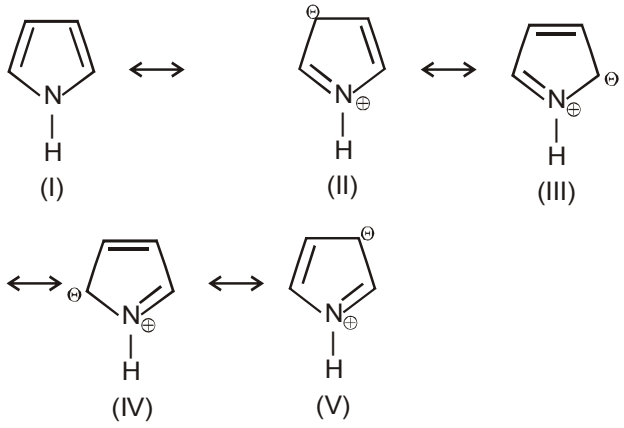
(A) (I = V) > (II = IV) > III

(B) (II = IV) > (I = V) > III

(C) (I = V) > III > (II = IV)

(D) III > (II = IV) > (I = V)

Sol.

17. 

(I) (II) (III) (IV) (V)

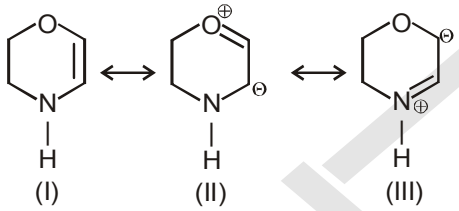
(A) (III = IV) > (II = V) > I

(B) I > (II = V) > (III = IV)

(C) I > (III = IV) > (II = V)

(D) (II = V) > (III = V) > I

Sol.

18. 

(I) (II) (III)

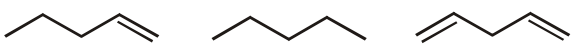
The least stable canonical structure among these is

(A) I (B) II (C) III

(D) all are equally stable

Sol.

19. Rank the following compounds in order of decreasing acidity.

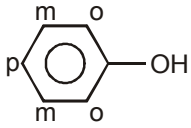


(I) (II) (III)

(A) III > II > I (B) I > II > III

(C) III > I > II (D) I > III > II

Sol.

20. 

In phenol, π-electron-density is maximum on

(A) ortho and meta positions

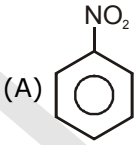
(B) ortho and para positions

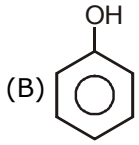
(C) meta and pera positions

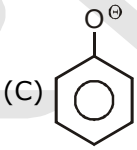
(D) none of these

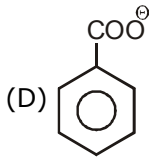
Sol.

21. Which of the following compounds has maximum electron density in ring ?

(A) 

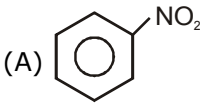
(B) 

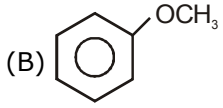
(C) 

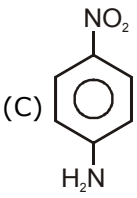
(D) 

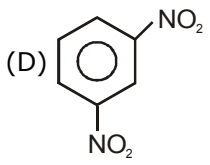
Sol.

22. In which of the following molecules π-electron density in ring is minimum?

(A) 

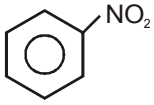
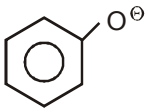
(B) 

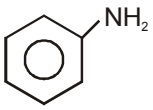
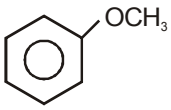
(C) 

(D) 

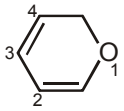
Sol.

23. In which of the following molecules π-electron density in ring is maximum?

(A)  (B) 

(C)  (D) 

Sol.

24. 

In this molecules, π-electron-density is more on

(A) C1 and C3 (B) C2 and C4
(C) C2 and C3 (D) C1 and C4

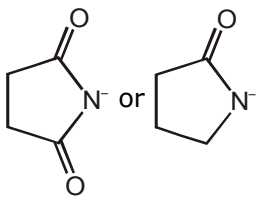
Sol.

25. In which of the following pairs, first species is more stable than second ?

(A) $CH_3CH_2O^-$ or $CH_3\overset{\overset{O}{\|}}{C}O^-$

(B) $CH_3\overset{\overset{O}{\|}}{C}\bar{C}HCH_2\overset{\overset{O}{\|}}{C}H$ or $CH_3\overset{\overset{O}{\|}}{C}\bar{C}H\overset{\overset{O}{\|}}{C}H_3$

(C) $CH_3\bar{C}HCH_2\overset{\overset{O}{\|}}{C}CH_3$ or $CH_3CH_2\bar{C}H\overset{\overset{O}{\|}}{C}CH_3$

(D) 

Sol.

26. CH_3COOH CH_3COONa CH_3CONH_2
(I) (II) (III)

Among these compounds, the correct order of resonance energy is

(A) I > II > III (B) III > II > I
(C) II > III > I (D) II > I > III

Sol.

27. Rank the following free radicals in order of decreasing stability

(I) $C_6H_5\dot{C}HC_6H_5$

(II) $C_6H_5 - \dot{C}H - CH = CH_2$

(III) $CH_3 - \dot{C}H - CH_3$ (IV) $C_6H_5 - \dot{C}H - CH_3$

(V) $CH_3CH\ CHCH_2\dot{C}H_2$

(VI) $CH_3 - CH_2 - \underset{\underset{CH_3}{|}}{\dot{C}} - CH_3$

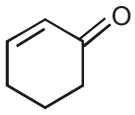
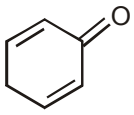
(A) I > II > IV > VI > III > V

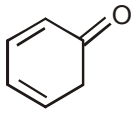
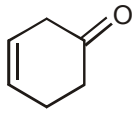
(B) VI > V > IV > III > II > I

(C) I > II > III > IV > V > VI

(D) I > IV > VI > V > II > III

Sol.

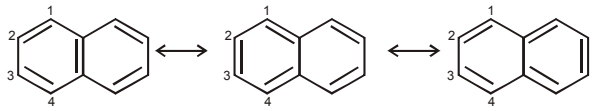
28. (I)  (II) 

(III)  (IV) 

Among these compounds, which one has maximum resonance energy ?

(A) I (B) II
(C) III (D) IV

Sol.

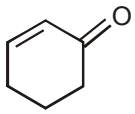
29. 

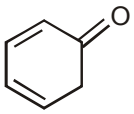
There are three canonical structures of napthalene. Examine them and find correct statement among the following:

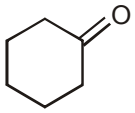
(A) All C–C bonds are of some length
(B) C1-C2 bond is shorter than C2-C3 bond.
(C) C1-C2 bond is longer than C2-C3 bond
(D) None.

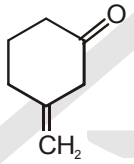
Sol.

30. Which of the following has longest C – O bond:

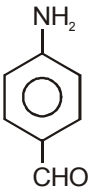
(A) 

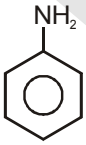
(B) 

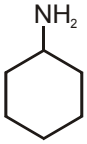
(C) 

(D) 

Sol.

31. (I) 

(II) 

(III) 

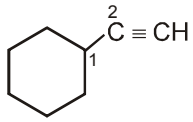
(IV) $CH_2 = NH$

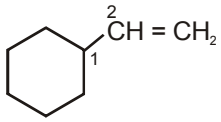
Among these compounds, the correct order of C – N bond length is :

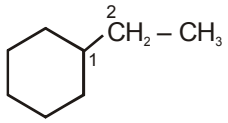
(A) IV > I > II > III
(B) III > I > II > IV
(C) III > II > I > IV
(D) III > I > IV > II

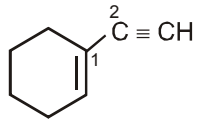
Sol.

32. C1 – C2 bond is shortest in

(A) 

(B) 

(C) 

(D) 

Sol.

33. Among the following molecules, the correct order of C - C bond length is

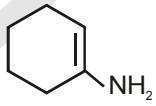
(A) $C_2H_6 > C_2H_4 > C_6H_6 > C_2H_2$
(B) $C_2H_6 > C_6H_6 > C_2H_4 > C_2H_2$ (C_6H_6 is benzene)
(C) $C_2H_4 > C_2H_6 > C_2H_2 > C_6H_6$
(D) $C_2H_6 > C_2H_4 > C_2H_2 > C_6H_6$

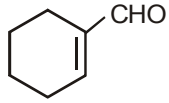
Sol.

34. In which of the following molecules resonance structutres are equivalent

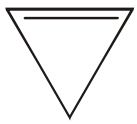
(A) $HCOO^{\ominus}$

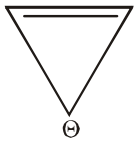
(B) $CH_2 = CH - CH = CH_2$

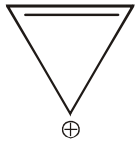
(C) 

(D) 

Sol.

35. (I) 

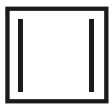
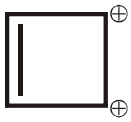
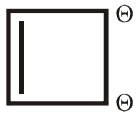
(II) 

(III) 

Which of these cyclopropene systems is aromatic

(A) I
(B) II
(C) III
(D) all of these

Sol.

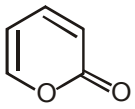
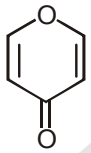
36. (I)  (II)  (III) 

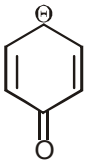
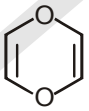
Which of these species is anti-aromatic ?

(A) I only (B) II only
(C) III only (D) both II and III

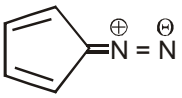
Sol.

37. Which of the following compouds is not aromatic

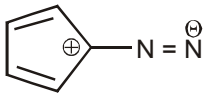
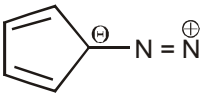
(A)  (B) 

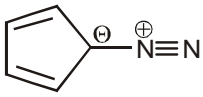
(C)  (D) 

Sol.

38. 

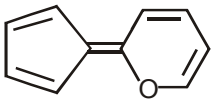
The most stable canonical structure of this molecule is

(A)  (B) 

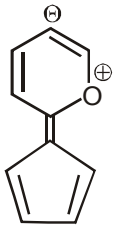
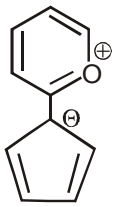
(C) 

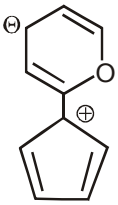
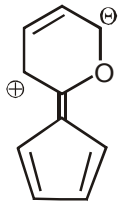
(D) All are equally stable

Sol.

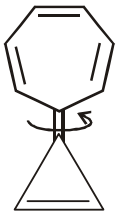
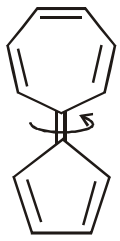
39. 

The most stable canonical structure of this molecule is

(A)  (B) 

(C)  (D) 

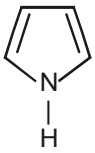
Sol.

40. (I)  (II)  (III) 

The barrier for rotation about the indicated bonds will be maximum in which of these three compounds ?

(A) I (B) II
(C) III (D) same in all

Sol.

41. (I)  (II)  (III) 

The aromatic character is maximum in which of these three compounds ?

(A) I (B) II
(C) III (D) same in all

Sol.

42. Find out the hybridisation state of carbon atoms in given compounds from left to right.

$CH_3 - CH = CH - CH = C = CH - C \equiv C - CH_3$

(A) $sp^3\ sp^2\ sp^2\ sp^2\ sp\ sp^2\ sp\ sp\ sp^3$
(B) $sp^3\ sp^2\ sp^2\ sp\ sp\ sp\ sp\ sp\ sp^3$
(C) $sp^3\ sp^2\ sp^2\ sp^2\ sp^2\ sp^2\ sp\ sp\ sp^3$
(D) $sp^3\ sp\ sp\ sp^2\ sp\ sp^2\ sp\ sp\ sp^3$

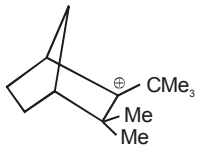
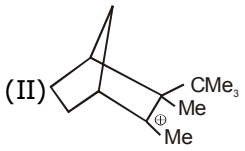
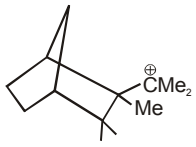
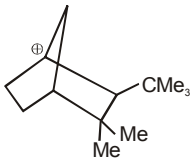
Sol.

43. Total number of σ and π-bonds are in naphthalene is

(A) 5π and 18σ (B) 6π and $19\ \sigma$
(C) 5π and 19σ (D) 7π and 26σ

Sol.

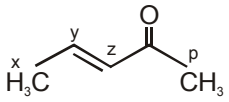
44. Writecorrect order of stability of following carbocations:

(I) 
(II) 
(III) 
(IV) 

(A) I > II > III > IV (B) III > II > I > IV
(C) III > I > II > IV (D) III > II > IV > I

Sol.

45. The abstraction of proton will be fastest, in which carbon in the following compound



(A) x (B) y
(C) z (D) p

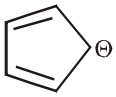
Sol.

46. Number of π-electron in $(C_4H_4)^{2-}$ is

(A) 2 (B) 4
(C) 6 (D) 8

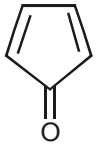
Sol.

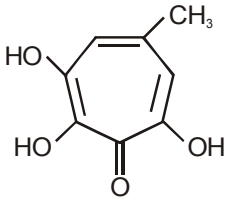
47. Identify the odd species out Which of the species among the following is different from others ?

(A) 
(B) 
(C) 
(D) 

Sol.

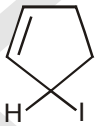
48. Which one of the following carbonyl compound when treated with dilute acid forms the more stable carbocation ?

(A) $CH_3 - \overset{\overset{O}{\|}}{C} - CH_3$ (B) 

(C)  (D) $C_6H_5 - \overset{\overset{O}{\|}}{C} - C_6H_5$

Sol.

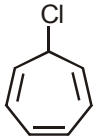
49. The order of the rate of formation of carbocations from the following iodo compound is:

(I)  (II)  (III) 

(A) I > II > III (B) I > III > II
(C) III > II > I (D) II > III > I

Sol.

50. Write correct order of reactivity of following halogen derivatives towards $AgNO_3$.

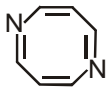
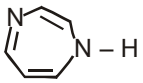
(I)  (II) $CH_2 = CH - Cl$ (III) $Et_3C - Cl$

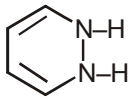
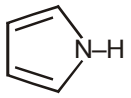
(IV) $PhCH_2Cl$ (V) $Ph_3C - Cl$

(A) I > V > IV > III > II
(B) V > IV > I > III > II
(C) V > I > IV > III > II
(D) I > V > III > IV > II

Sol.

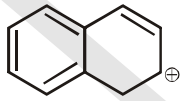
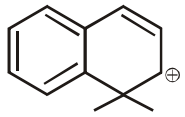
51. Which of the following heterocyclic compounds would have aromatic character ?

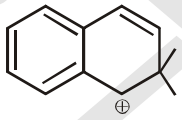
(A)  (B) 

(C)  (D) 

Sol.

52. Arrange the following carbocations in the increasing order of their stability.

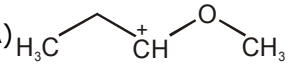
(I)  (II) 

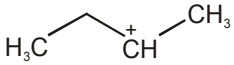
(III) 

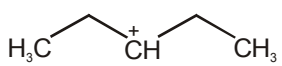
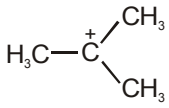
(A) I > II > III (B) I > II = III
(C) I > III > II (D) III > I > II

Sol.

53. Which of the following carbocation will be more stable ?

(A) 

(B) 

(C)  (D) 

Sol.

54. **Statement-1:** $Me - \overset{\oplus}{C}H_2$ is more stable than MeO $- CH_2^{\oplus}$

Statement-2: Me is a +I group where as MeO is a –I group.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT correct explanation for statement-1.

(C) Statement1 is false, statement-2 is true.

(D) Statement1 is true, statement-2 is false.

Sol.

55. When $-CH_3$, $CH_3-\underset{CH_3}{\underset{|}{CH}}-$ and $CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-$ groups are introduced on benzene ring then correct order of their inductive effect is

(A) $CH_3- > CH_3-\underset{CH_3}{\underset{|}{CH}}- > CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-$

(B) $CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}- > CH_3-\underset{CH_3}{\underset{|}{CH}}- > CH_3-$

(C) $CH_3-\underset{CH_3}{\underset{|}{CH}}- > CH_3 > CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-$

(D) $CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}- > CH_3- > CH_3-\underset{CH_3}{\underset{|}{CH}}-$

Sol.

56. The correct order of increasing basic nature of the bases NH_3, CH_3NH_2 and $(CH_3)_2NH$ is gas phase

(A) $NH_3 < CH_3NH_2 < (CH_3)_2NH$
(B) $CH_3NH_2 < (CH_3)_2NH < NH_3$
(C) $CH_3NH_2 < NH_3 < (CH_3)_2NH$
(D) $(CH_3)_2NH < NH_3 < CH_3NH_2$

Sol.

57. Consider the acidity of the carboxylic acids

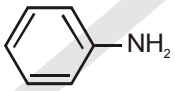
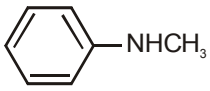
(a) PhCOOH (b) o–$NO_2C_6H_4COOH$
(c) p-$NO_2C_6H_4COOH$ (d) m-$NO_2C_6H_4COOH$

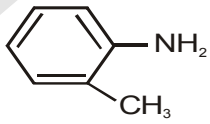
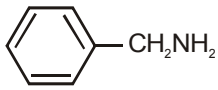
Which of the following order is correct ?

(A) a > b > c > d (B) b > d > c > a
(C) b > d > a > c (D) b > c > d > a

Sol.

58. Which of the following is the strongest base

(A)  (B) 

(C)  (D) 

Sol.

59. Amongst the following the most basic compound is

(A) Aniline (B) Benzylamine
(C) p-nitroaniline (D) Acetanilide

Sol.

60. The increasing order of stability of the following free radicals is

(A) $(C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$

(B) $(C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C} < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$

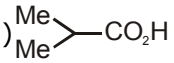
(C) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H$

(D) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C}$

Sol.

61. The correct order of increasing acid strength of the compounds

(a) CH_3CO_2H (b) $MeOCH_2CO_2H$

(c) CF_3CO_2H (d) 

(A) d < a < c< d (B) d < a < b < c
(C) a < d < c < b (D) b < d < a < c

Sol.

62. Which one of the following is the strongest base in aqueous solution ?

(A) Trimethylamine (B) Aniline
(C) Dimethylamine (D) Methylamine

Sol.

63. Arrange the carbonions,
$(CH_3)_3\bar{C}$, $\bar{C}Cl_3$, $(CH_3)_2\bar{C}H$, $C_6H_5\bar{C}H_2$ in order of their decreasing stability

(A) $(CH_3)_2\bar{C}H > \bar{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_3\bar{C}$

(B) $\bar{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_2\bar{C}H > (CH_3)_3\bar{C}$

(C) $(CH_3)_3\bar{C} > (CH_3)_2\bar{C}H > C_6H_5\bar{C}H_2 > \bar{C}Cl_3$

(D) $C_6H_5\bar{C}H_2 > \bar{C}Cl_3 > (CH_3)_3\bar{C} > (CH_3)_2\bar{C}H$

Sol.

64. Consider the following carbanions

(i) $CH_3-\overset{\ominus}{C}H_2$ (ii) $CH_2=\overset{\ominus}{C}H$

(iii) $CH\equiv\overset{\ominus}{C}$

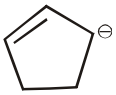
Correct order of stabilityof these carboanions in decreasing order is

(A) i > ii > iii (B) ii > i > iii
(C) iii > ii > i (D) iii > i > ii

Sol.

65. The order of stability of the following carbanion is

(I) $CH_3\overset{\ominus}{C}H_2$ (II) 

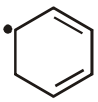
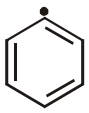
(III)  (IV) 

(A) I > II > III > IV (B) I > III > II > IV
(C) IV > III > II > I (D) III > IV > I > II

Sol.

66. Rank thefollowing radicals in order of decreasing stability

(I)  (II) 

(III)  (IV) 

(A) III > II > I > IV (B) III > IV > I > II
(C) II > III > I > IV (D) IV > II > I > III

Sol.

67. Arrange in decreasing pK_a

(a) $F - CH_2CH_2 COOH$

(b) $Cl - \underset{\underset{Cl}{|}}{CH} - CH_2 - COOH$

(c) $F - CH_2 - COOH$

(d) $Br - CH_2 - CH_2 - COOH$

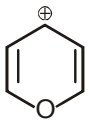
Correct answer is

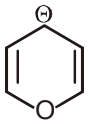
(A) b > d > a > c (B) a > c > d > b

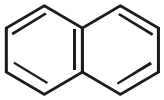
(C) c > b > a > d (D) d > b > a > c

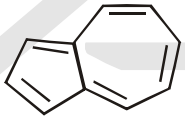
Sol.

68. Which of the following species is not aromatic ?

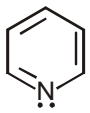
(A) 

(B) 

(C) 

(D) 

Sol.

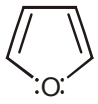
69. 

Nitrogen atom of pyridine is

(A) sp^3 hybridized (B) sp^2 hybridized

(C) sp hybridized (D) Not hybridized

Sol.

70. 

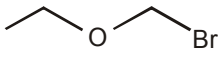
Oxygen atom of furan is

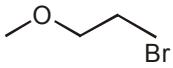
(A) sp^3 hybridized (B) sp^2 hybridized

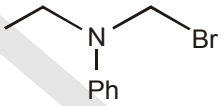
(C) sp hybridized (D) Not hybridized

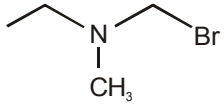
Sol.

71. Ease of ionization to produce carbocation and bromide ion under the treatment of $Ag^{\oplus}$ will be maximum in which of the following compounds?

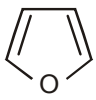
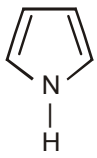
(A) 

(B) 

(C) 

(D) 

Sol.

72. (I)  (II)  (III) 

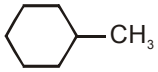
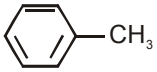
Which of the following choice is the correct order of resonance energy of these molecules ?

(A) I > II > III (B) II > I > III

(C) III > II > I (D) III > I > II

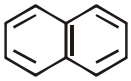
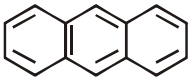
Sol.

73. Which can lose a proton more readily, a methyl group bonded to cyclohexane or a methyl group bonded to bezene ?

(I)  (II) 

(A) I > II (B) II > I
(C) equal (D) None

Sol.

74. (I)  (II)  (III) 

Among these aromatic compounds the correct order of resonance eneergy per ring is

(A) I > II > III (B) III > II > I
(C) III > I > II (D) II > I > III

Sol.

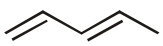
75. (I)  (II) 

Which of the following orders is correct for the resonance energy of these two compounds ?

(A) I > II (B) II > I

(C) I = II
(D) there is nothing like π-electron energy

Sol.

76. (I)  (II) 

Which of the following order is correct for the resonance energy of these two compounds ?

(A) I > II (B) II > I

(C) I = II
(D) there is nothing like π-electron energy

Sol.

77. (I) $CH_2 = CH - \overset{\oplus}{C}H_2$ (II) 

Which of the following order is correct for resonance energy of these cation

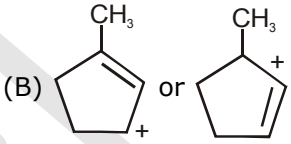
(A) I > II (B) II > I
(C) I = II

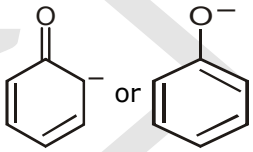
(D) there is nother like π-election energy

Sol.

78. Contribution of second resonating structure is more than first ?

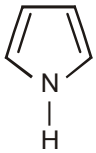
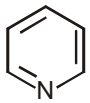
(A) $CH_3CH = CHCH_2^+$ or $CH_3CH^+CH = CH_2$

(B) 

(C) 

(D) All of these

Sol.

79. (I)  (II)  (III) 

The aromatic character is maximum in which of these three compounds ?

(A) I (B) II
(C) III (D) Same in all

Sol.

EXERCISE – II OBJECTIVE PROBLEMS (JEE ADVANCED)

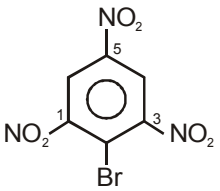
1. H – O – C ≡ N (Cyanic acid) H – N = C = O (Isocyanic acid)

Loss of proton from these two acids produces

(A) same anion (B) different anions
(C) same cation (D) different cations

Sol.

2. Which of the following statements would be true about this compound:



(A) All three C – N bonds are of same length.

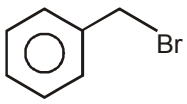
(B) C1 – N and C3 – N bonds are of same length but shorter than C5 – N bond

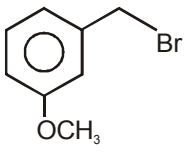
(C) C1 – N and C3 – N bonds are of same length but longer than C5 – N bond

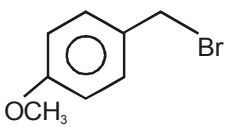
(D) C1 – N and C3 – N bonds are of different length but bot are longer than C5 – N bond.

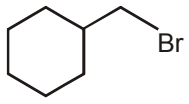
Sol.

3. Ease of ionization to produce carbocation and bromide ion under the treatment of $Ag^{\oplus}$ will be maximum in whichof the following compounds ?

(A) 

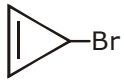
(B) 

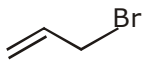
(C) 

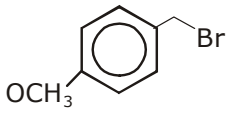
(D) 

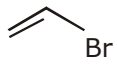
Sol.

4. Ease of ionization to produce carbocation and bromide ion under the treatment of $Ag^{\oplus}$ will be maximum in whichof the following compounds ?

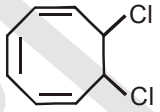
(A) 

(B) 

(C) 

(D) 

Sol.

5. 

P will be

(A) 

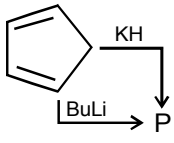
(B) 

$2SbCl_6$

(C) 

(D) mixture of (a) and (b)

Sol.

6. 

P will be

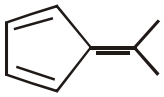
(A) 

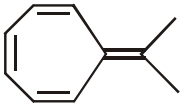
(B) 

(C) mixture of (A) & (B) (D) none of these

Sol.

7. Which one of the following statements is **True**:

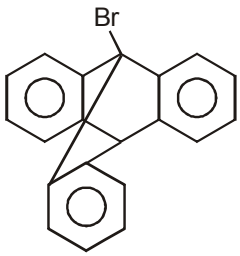
(1) 

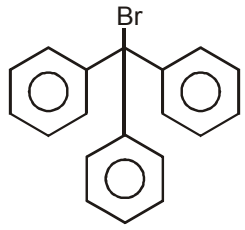
(2) 

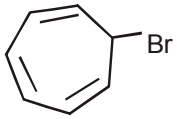
(A) PhLi adds to both compound with equal ease
(B) PhLi does not add to either of the compound
(C) PhLi react readily with 1 but does not add to 2
(D) PhLi react readility with 2 but does not add to 1

Sol.

8. Correct order of rate of hydrolysis or rate of reaction toward $AgNO_3$ for following compounds is

(I) 

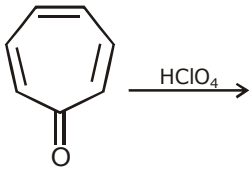
(II) 

(III) 

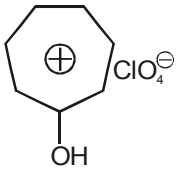
(IV) 

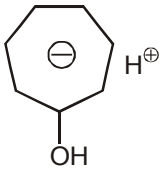
(A) III > II > IV > I
(B) I > II > III > IV
(C) III > I > II > IV
(D) III > II > I > IV

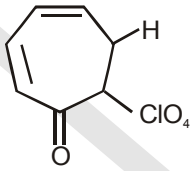
Sol.

9. 

P will be

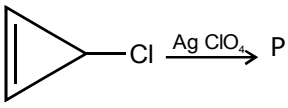
(A) 

(B) 

(C) 

(D) Mixture of (A) & (B)

Sol.

10. 

P

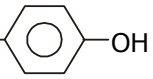
(A) 

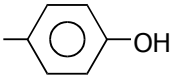
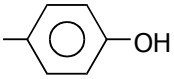
(B) 

(C) Mixture of (A) & (B)
(D) None of these

Sol.

11. Arrange the given phenols in their decreasing order of acidity:

(I) C_6H_5–OH (II) 

(III)  (IV) 

Select the correct answer from the given code:

(A) IV > III > I > II (B) IV > II > III > I

(C) IV > III > II > I (D) IV > I > III > II

Sol.

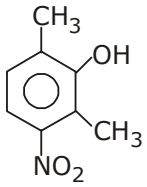
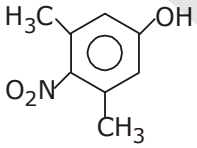
12. Which one of the following is the most acidic?

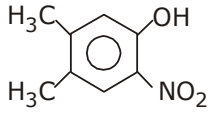
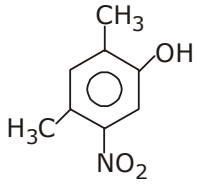
(A)  (B) 

(C)  (D) $CH_2=CH-CH_3$

Sol.

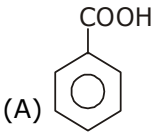
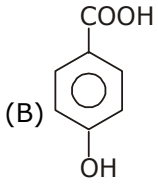
13. Which one of the following phenols will show highest acidity?

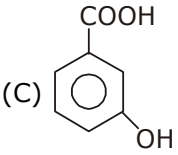
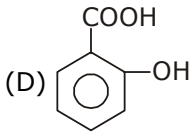
(A)  (B) 

(C)  (D) 

Sol.

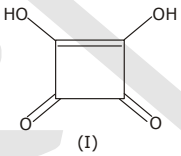
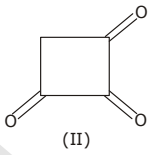
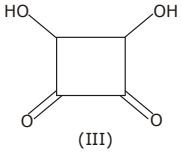
14. Which of the following is weakest acid?

(A)  (B) 

(C)  (D) 

Sol.

15. The correct pKa order of the follwoing acids is :

 (I)  (II)  (III)

(A) I > II > III (B) III > II > I

(C) III > I > II (D) I > III > II

Sol.

16. Arrange pH of the given compounds in decreasing order:

(1) Phenol (2) Ethyl alcohol

(3) Formic acid (4) Benzoic acid

(A) 1 > 2 > 3 > 4 (B) 2 > 1 > 4 > 3

(C)3 > 2 > 4 > 1 (D) 4 > 3 > 1 > 2

Sol.

17. Arrange acidity of given compounds in decreasing order:

(I) $CH_3–NH–CH_2–CH_2–OH$

(II) $CH_3–NH–CH_2–CH_2–CH_2–OH$

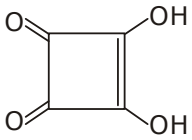
(III) $(CH_3)_3\overset{\oplus}{N}–CH_2–CH_2–OH$

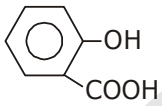
(A) III > I > II (B) III > II > I

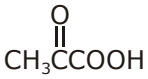
(C) I > II > III (D) II > I > III

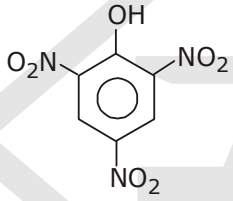
Sol.

18. Consider the following compound

(A) 

(B) 

(C) 

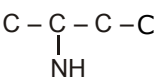
(D) 

Which of the above compounds reacts with $NaHCO_3$ giving CO_2

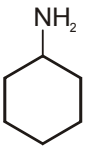
Sol.

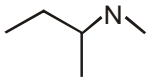
More than one Correct

19. Which of the following is a 2° Amine ?

(A) 

(B) 

(C) 

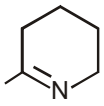
(D) 

Sol.

20. Identify electron - withdrawing groups in resonance among the following:

(a) – COOH (b) – $CONHCH_3$

(c) – COCl (d) – CN

(e) – O – CH = CH_2 (f) 

Sol.

21. Identify electron - donating groups in resonance among the following:

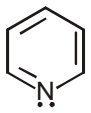
(a) – $CONH_2$ (b) – NO_2

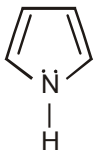
(c) – $OCOCH_3$ (d) – $COOCH_3$

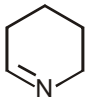
(e) – CHO (f) – $NHCOCH_3$

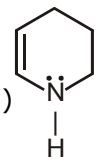
Sol.

22. In which of the following lone-pair indicated is involved in resonance :

(a) 

(b) 

(c) 

(d) 

(e) $CH_2 = CH – CH_2^-$

(f) $CH_2 = CH - CH = \overset{\bullet\bullet}{NH}$

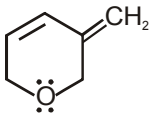
Sol.

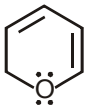
23. In which of the following lone-pair indicated is not involved in resonance :

(a) $CH_2 = CH - \ddot{N}H - CH_3$

(b) $CH_2 = CH - CH = \ddot{O}$

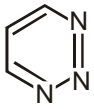
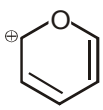
(c) $CH_2 = CH - \ddot{O} - CH = CH_2$

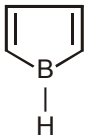
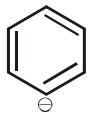
(d) $CH_2 = CH - C \equiv \ddot{N}$ (e) 

(f) 

Sol.

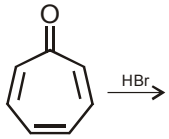
24. Aromatic compounds are:

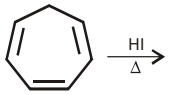
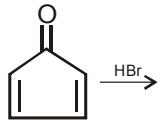
(A)  (B) 

(C)  (D) 

Sol.

25. Which of the following reactions give aromatic compound ?

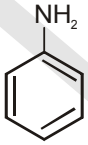
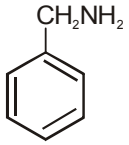
(A)  (B) 

(C)  (D) 

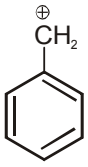
Sol.

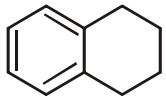
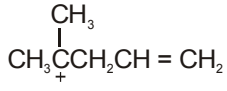
26. In which of the following molecules resonance takes place through out the entire system.

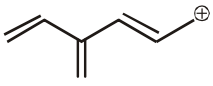
(A) $CH_3CH_2NHCH_2CH = CH_2$

(B)  (C) 

(D) $CH_2 = CHCH_2CH = CH_2$

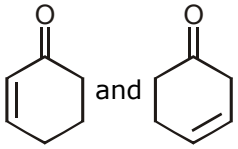
(E)  (F) 

(G)  (H) 

(I) 

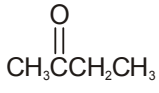
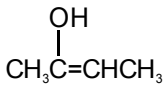
Sol.

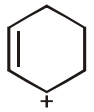
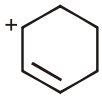
27. Which of the following pairs of structures are resonance contributors ?

(A)  and

(B) $CH_3CH = CH\overset{+}{C}HCH = CH_2$ and

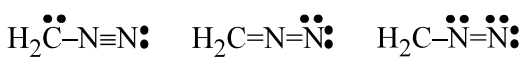
$CH_3\overset{+}{C}HCH = CHCH = CH_2$

(C)  and 

(D)  and 

Sol.

28. Consider structural formulas A, B and C:



(A) (B) (C)

(a) Are A, B and C constitutional isomers, or are they resonance forms?

(b) Which structures have a negatively charged carbon?

(c) Which structures have a positively charged carbon?

(d) Which structures have a positively charged nitrogen?

(e) Which structures have a negatively charged nitrogen?

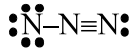
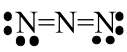
(f) What is the net charge on each structure?

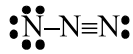
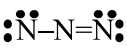
(g) Which is a more stable structure, A or B? Why?

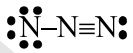
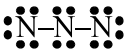
(h) Which is a more stable structure, B or C? Why?

Sol.

29. In each of the following pairs, determine whether the two represent resonance forms of a single species or depict different substances. If two structures are not resonance froms, explain why.

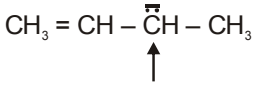
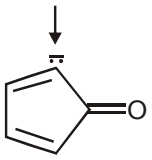
(a)  and 

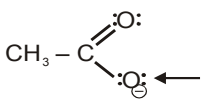
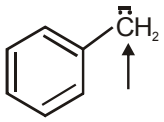
(b)  and 

(c)  and 

Sol.

30. Determine the hybridization around the indicated atom in the following anion.

(A)  (B) 

(C)  (D) 

Sol.

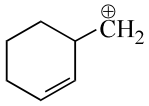
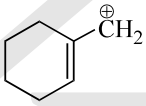
31. Using hybridization, predict how the bond legnth of the C – C σ bond in HC ≡ C – C ≡ CH should compare with the C – C σ bonds in CH_3CH_3 and $CH_2 = CH - CH = CH_2$.

Sol.

32. In each of the following pairs of ions which ion is more stable:

(a) (I) $C_6H_5-\overset{\oplus}{C}H_2$ and (II) $CH_2=CH-\overset{\oplus}{C}H_2$

(b) (I) $CH_3-\overset{\oplus}{C}H_2$ and (II) $CH_2 = \overset{\oplus}{C}H$

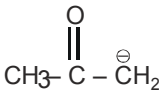
(c) (I)  and (II) 

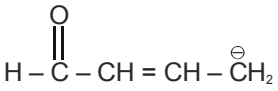
(d) (I) $CH_3-\underset{\underset{\oplus}{|}}{\overset{|}{C}}(CH_3)-CH_3$ and

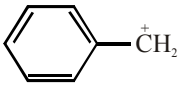
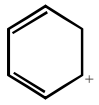
(II) $CH_3-\underset{\underset{\oplus}{|}}{\overset{|}{C}}(CH_3)-N(CH_3)-CH_3$

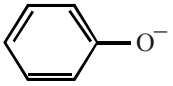
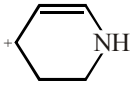
Sol.

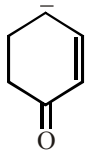
33. Draw the resonance forms to show the delocalization of charges in the following ions

(a) 

(b) 

(c)  (d) 

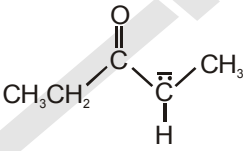
(e)  (f) 

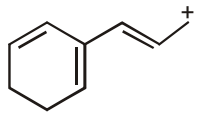
(g)  (h) 

(i) $CH_3 - CH = CH - CH = CH - \overset{+}{C}H - CH_3$

(j) $CH_3 - CH = CH - CH = CH - \overset{+}{C}H_2$

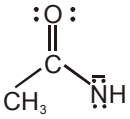
(k) $CH_2 = CH - \ddot{C}H - CH = CH_2$

(l) 

(m) $CH_3 - \overset{+}{C}H - \ddot{C}l:$ (n) 

Sol.

34. Draw a second resonance structure and the hybrid for each species, and then rank the two resonance strcutures and the hybrid in order of increasing stability

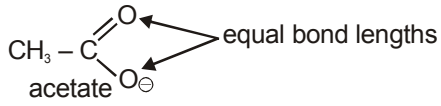
(A) $(CH_3)_2 - \overset{+}{C} - \ddot{N}H_2$ (B) 

Sol.

35. For acetic acid (CH_3CO_2H): (a) Draw three resonance structures; (b) draw a structure for the resonance hybrid;s (c) rank the three resonance structures and the resonance hybrid in order of increasing energy.

Sol.

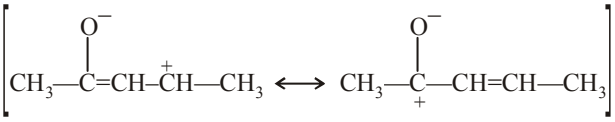
36. Use resonance theory to explain why both C – O bond lengths are equal in the acetate anion.

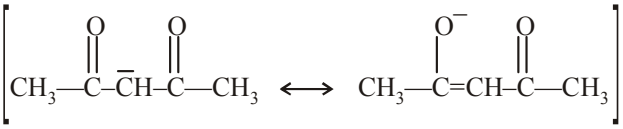


Sol.

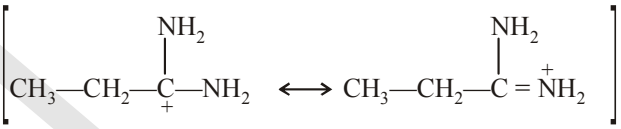
37. In the following sets of resonance forms, label the major and minor contributors and state which structures would be of equal energy. Add any missing resonance forms.

(a) 

(b) 

(c) 

(d) $[CH_3 - \overline{C}H - CH = CH - NO_2 \longleftrightarrow CH_3 - CH = CH - \overline{C}H - NO_2]$

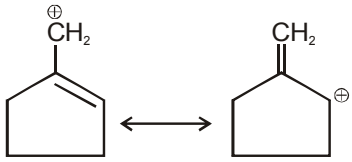
(e) 

Sol.

38. From each set of resonance structure that follow, designate the one that would contribute most to the hybrid and explain your choice.

(a) 

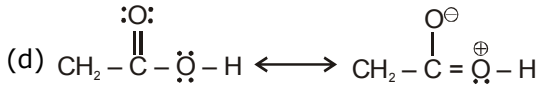
(i) (ii)

(b) 

(i) (ii)

(c) $\overset{\oplus}{C}H_2 - \ddot{N}(CH_3)_2 \longleftrightarrow CH_2 = \overset{\oplus}{N}(CH_3)_2$

(i) (ii)

(d) 

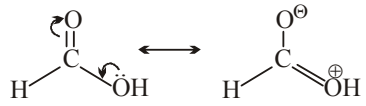
(i) (ii)

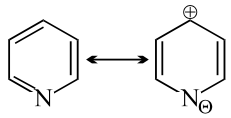
(e) $: NH_2 - C \equiv N \longleftrightarrow \overset{\oplus}{N}H_2 = C = N^{\ominus}$

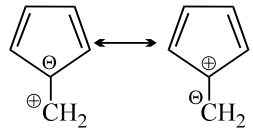
(i) (ii)

Sol.

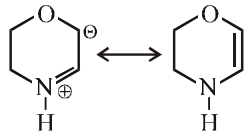
39. Identify more stable canonical structure in each of the following pairs :

(a) 

(b) 

(c) 

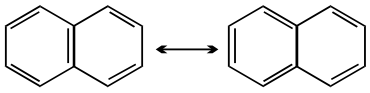
(d) $\overset{\oplus}{C}H_2 - CH = CH - \overset{\Theta}{O} \longleftrightarrow CH_2 = CH - CH = O$

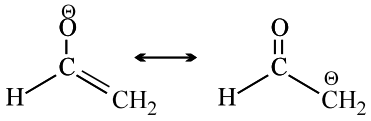
(e) 

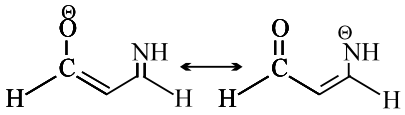
Sol.

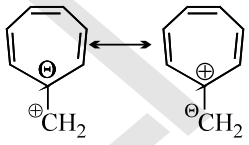
40. Identify less stable canonical structure in each of the following pairs :

(a) $\overset{\oplus}{C}H_2 - O - CH_3 \longleftrightarrow CH_2 = \overset{\oplus}{O} - CH_3$

(b) 

(c) 

(d) 

(e) 

Sol.

41. Which of the following statements is (are) true about resonance.

(a) Resonance is an intramolecular process.

(b) Resonance involves delocalization of both σ and π electrons.

(c) Resonance involves delocalization of π electrons and lone pair only.

(d) Resonance decreases potential energy of a molecule.

(e) Resonance has no effect on the potential energy of a molecule.

(f) Resonance is the only way to increase molecular stability.

(g) Resonance is not the only way to increase molecular stability.

(h) Any resonating molecule is always more stable than any nonresonating molecule.

(i) The canonical structure explains all features of a molecule.

(j) The resonance hybrid explains all features of a molecule.

(k) Resonating structures are real and resonance hybrid is imaginary.

(l) Resonance hybrid is real and resonating structures are imaginary.

(m) Resonance hybrid is always more stable than all canonical structures.

Sol.

42. Resonance energy will be more if

(a) canonical structures are equivalent than if canonical structures are non-equivalent.

(b) molecule is aromatic than if molecule is not aromatic.

Sol.

43. A canonical structure will be more stable if

(a) it has more number of π bonds than if it has less number of π bonds.

(b) the octate of all atoms are complete than if octate of all atoms are not complete.

(c) it involves cyclic delocalization of $(4n + 2)\ \pi$ – electrons than if it involves acyclic delocalization of $(4n + 2)\ \pi$ – electrons.

(d) it involves cyclic delocalization $(4n)\ \pi$ – electrons than if it involves acyclic delocalizationof $(4n)\ \pi$ – electrons.

(e) +ve charge is on more electronegative atom than if +ve charge is on less electronegative atoms.

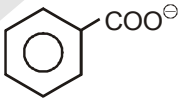
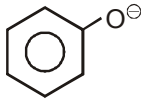
(f) –ve charge is on more electronegative atom than if –ve charge is on less electronegative atom.

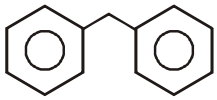
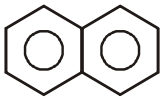
Sol.

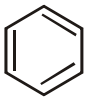
44. Which of the following pairs has higher resonance energy:

(a) CH_3COOH and CH_3COONa

(b) $CH_2 = CH - \overset{\ominus}{O}$ and $CH_2 = CH - OH$

(c)  and 

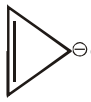
(d)  and 

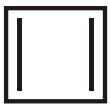
(e)  and $CH_2 = CH - CH = CH - CH = CH_2$

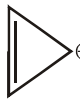
Sol.

45. Which of the following pairs has less resonance energy:

(a) CO_3^{2-} and $HCOO^-$

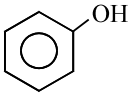
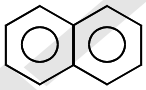
(b)  and $CH_2 = CH - CH_2^-$

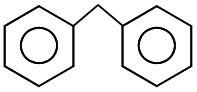
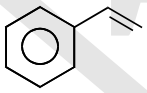
(c)  and $CH_2 = CH - CH = CH_2$

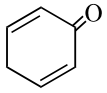
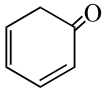
(d)  and $CH_2 = CH - CH_2^+$

Sol.

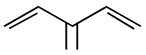
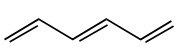
46. Which of the following pairs has higher resonance energy :

(a)  and 

(b)  and 

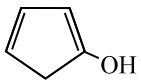
(c)  and 

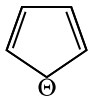
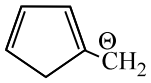
(d) $CH_2 = CH - OH$ and $CH_2 = CH - CH = CH - OH$

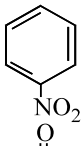
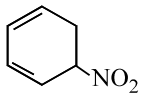
(e)  and 

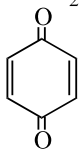
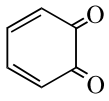
Sol.

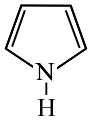
47. Which of the following pairs has less resonance energy :

(a)  and 

(b)  and 

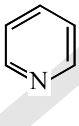
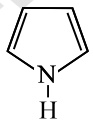
(c)  and 

(d)  and 

(e)  and 

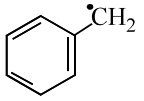
Sol.

48. Which of the following pairs has higher resonance energy :

(a)  and 

(b) $CH_2 = CH - O - CH = CH_2$ and $CH_2 = CH - NH - CH = CH_2$

(c) $CH_2 = CH - \overset{\Theta}{N}H$ and $HN = CH - \overset{\Theta}{N}H$

(d)  and $CH_2 = CH - \dot{C}H_2$

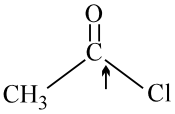
(e) $CH_2 = CH - F$ and $CH_2 = CH - Br$

Sol.

49. In which of the following pairs, indicated bond is of greater strength :

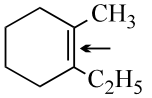
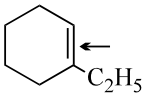
(a) CH_3-CH_2-Br and CH_3-CH_2-Cl

(b) $CH_3-CH=CH-Br$ and $CH_3-\underset{\underset{Br}{|}}{CH}-CH_3$

(c)  and CH_3-CH_2-Cl

(d) $CH_2=CH-CH=CH_2$ and

$CH_2=CH_2-CH_2-CH_3$

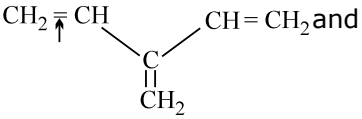
(e)  and 

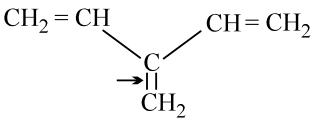
Sol.

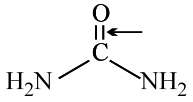
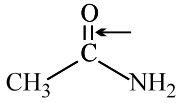
50. In which of the following pairs, indicated bond having less bond dissociation energy :

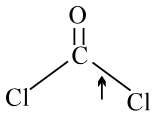
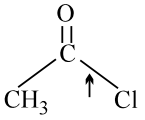
(a)  and $CH_2=CH_2$

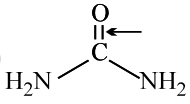
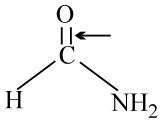
(b) $CH_3-C\equiv CH$ and $HC\equiv CH$

(c)  and



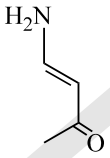
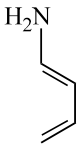
(d)  and 

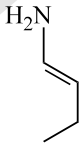
(e)  and 

(f)  and 

Sol.

51. Compare the C–N bond-length in the following species:

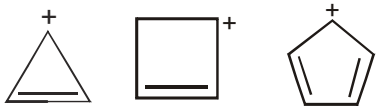
(i)  (ii) 

(iii) 

Sol.

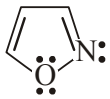
52. Rank the following sets of intermediates in increasing order of their stability given appropriate reasons for your choice

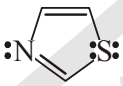
(a) $C_6H_5^+$, $p–NO_2(C_6H_4)^+$, $p–CH_3–(C_6H_4)^+$, $p–Cl–C_6H_4^+$

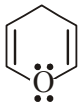
(b) 

Sol.

53. Explain why each compound is aromatic, antiaromatic or nonaromatic.

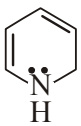
(a) 
isoxazole

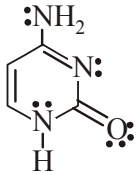
(b) 
1,3-thiazole

(c) 
pyran

(d) 
pyrylium ion

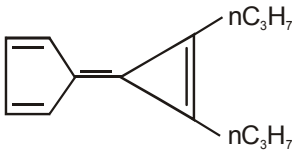
(e) 
γ-pyrone

(f) 
1,2-dihydropyridine

(g) 
cytosine

Sol.

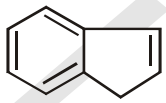
54. Ordinarily the barrier to rotation about a carbon-carbon double bond is quite high but compound A have a rotational barrier of only about 20 K cal / mol

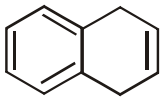


What is the reason for this ?

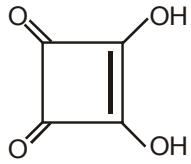
Sol.

55. Which is more acidic and why ?

(A) 

(B) 

Sol.

56. Square acid  is a diprotic acid with both protons being more acidic than acetic acid. In the di-anionafterthe loss of both protons all of the C-C bonds are the same length as well as all of the C-O bonds. Provide a explanaton for these observations.

Sol.

57. Match each alkene with the appropriate heat of combustion:

Heats of combustion (kJ/mol) : 5293 ; 4658; 4650; 4638; 4632

(a) 1-Heptene

(b) 2,4-Dimethyl-1-pentene

(c) 2,4-Dimethyl-2-pentene

(d) 4,4-Dimethyl-2-pentene

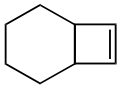
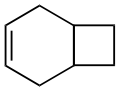
(e) 2,4,4-Trimethyl-2-pentene

Sol.

58. Choose the more stable alkene in each of the following pairs. Explain your reasoning.

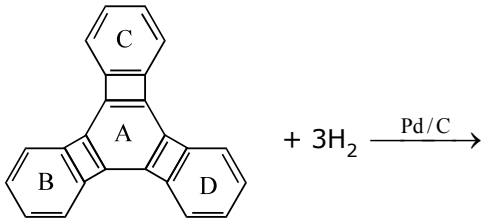
(a) 1-Methylcyclohexene or 3-methylcyclohexene

(b) Isopropenylcyclopentane or allylcyclopentane

(c)  or 

Sol.

59. Consider the given reaction:

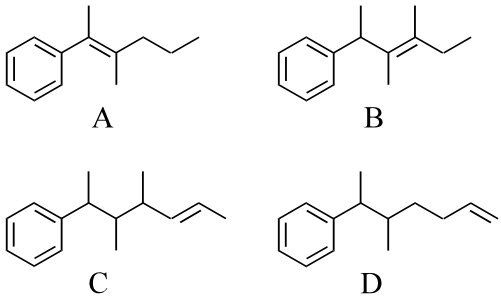


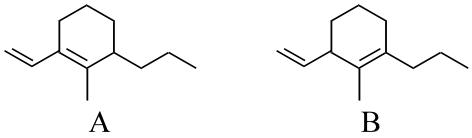
In the above reaction which one of the given ring will undergo reduction?

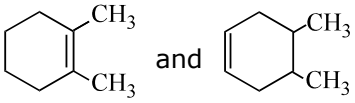
Sol.

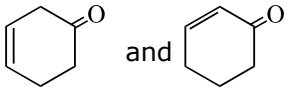
60. Compare heat of hydrogenation (Decreasing order)

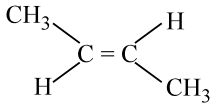
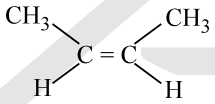
(a) heat of hydrogenation

(i) 

(ii)  A B C D E

(b)  and

(c)  and

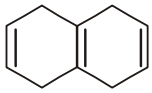
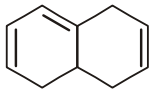
(d)  and 

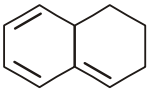
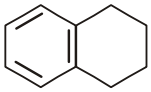
(e) $CH_2 = CH - CH\begin{matrix}CH_3\\CH_3\end{matrix}$ and

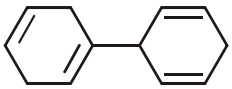
$CH_2 = C\begin{matrix}CH_3\\CH_2-CH_3\end{matrix}$

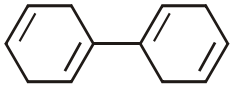
Sol.

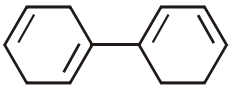
61. (I) Stability order and (II) heat of hydrogenation orders.

(A) (i)  (ii) 

(iii)  (iv) 

(B) (i) 

(ii) 

(iii) 

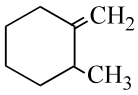
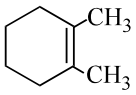
Sol.

62. Among the following pairs identify the one which gives higher heat of hydrogenation :

(a)  and 

(b)  and 

(c) $CH_3 - CH = CH - CH_3$ and $CH_3 - CH_2 - CH = CH_2$

(d)  and 

Sol.

63. Discuss the following observations:

(a) C–Cl bond in vinyl chloride is stronger than in chloroethane.

(b) Carbon-carbon bond length in ethene is shorter than in $CH_2 = CHOCH_3$

(c) CH_3SH is stronger acid than CH_3OH

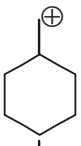
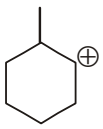
(d) $CH_3CH_2NH_2$ is stronger base than $CH_2 = CHNH_2$.

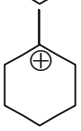
Sol.

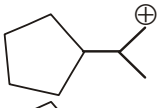
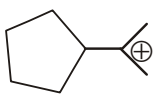
64. Write stability order of following intermediates:

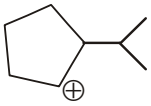
(i) (a) $CH_3-\overset{\oplus}{C}H_2$ (b) $CH_3-\overset{\oplus}{C}H-CH_3$

(c) $CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\oplus$

(ii) (a)  (b) 

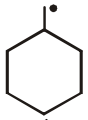
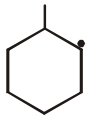
(c) 

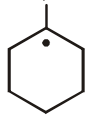
(iii) (a)  (b) 

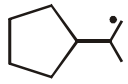
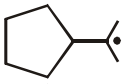
(c) 

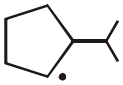
(iv) (a) $CH_3-\dot{C}H_2$

(b) $CH_3-\dot{C}H-CH_3$ (c) $CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\bullet$

(v) (a)  (b) 

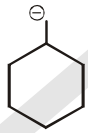
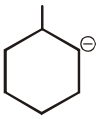
(c) 

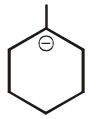
(vi) (a)  (b) 

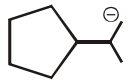
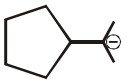
(c) 

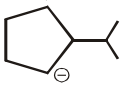
(vii) (a) $HC\equiv\overset{\Theta}{C}$ (b) $CH_3-\overset{\Theta}{C}H-CH_3$

(c) $CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\Theta$

(viii) (a)  (b) 

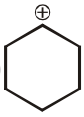
(c) 

(ix) (a)  (b) 

(c) 

(x) (a)  (b) 

(c) 

(d) 

(xi) (a) $HC \equiv \overset{\ominus}{C}$ (b) $CH_2 = \overset{\Theta}{C}H$

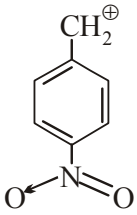
(c) $CH_3 - \overset{\Theta}{C}H_2$

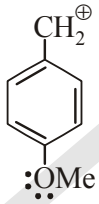
(xii) (a) $HC \equiv \overset{\bullet}{C}$ (b) $CH_2 = \overset{\bullet}{C}H$

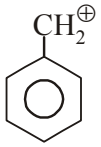
(c) $CH_3 - \overset{\bullet}{C}H_2$

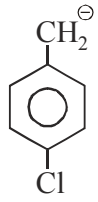
Sol.

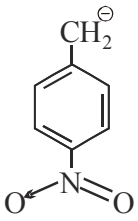
65. Write stability order of following intermediates:

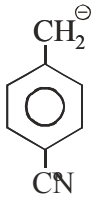
(i) (a) 

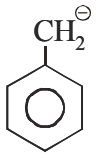
(b) 

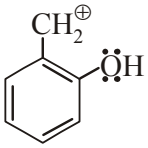
(c) 

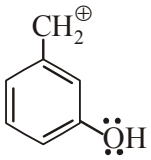
(ii) (a) 

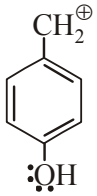
(b) 

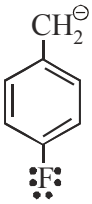
(c) 

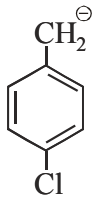
(d) 

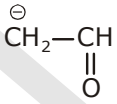
(iii) (a) 

(b) 

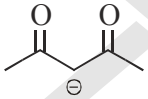
(c) 

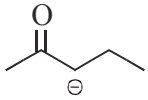
(iv) (a) 

(b) 

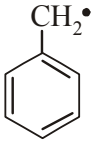
(v) (a) 

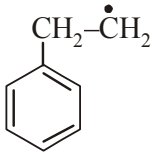
(b) $\overset{\Theta}{C}H_2 - CH_3$

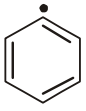
(vi) (a) 

(b) 

(c) 

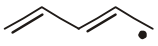
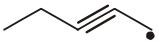
(vii) (a) 

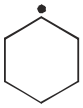
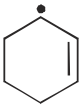
(b) 

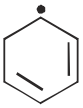
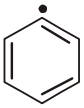
(c) 

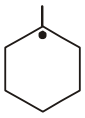
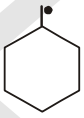
(viii) (a)  (b) 

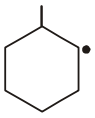
(c) 

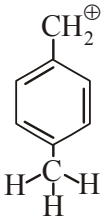
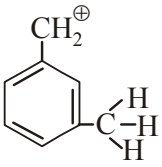
(ix) (a)  (b) 

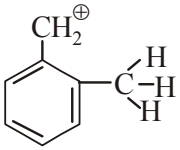
(x) (a)  (b) 

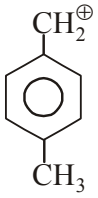
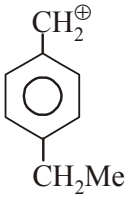
(c)  (d) 

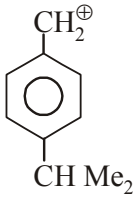
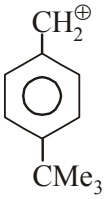
(xi) (a)  (b) 

(c) 

(xii) (a)  (b) 

(c) 

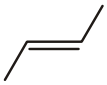
(xiii) (a)  (b) 

(c)  (d) 

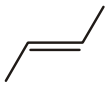
66. Write increasing order of heat of hydrogenation :

(i) (a)  (b) 

(ii) (a)  (b) 

(c)  (d) 

(iii) (a) (b) 

(c)  (d) 

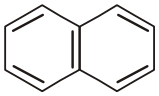
(e) 

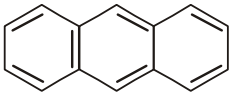
(iv) (a)  (b) 

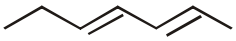
(c) 

(v) (a)  (b) 

(c)  (HOH per π bond)

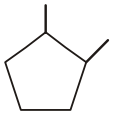
(vi) (a)  (b) 

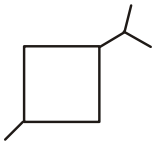
(c)  (HOH per benzene ring)

(vii) (a)  (b) 

(viii) (a)  (b) 

67. Give decreasing order of heat of combustion (HOC):

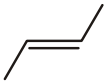
(i) (a)  (b) 

(c) 

(ii) (a)  (b) 

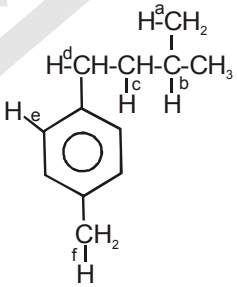
(c)  (d) 

(iii) (a)  (b) 

(iv) (a)  (b) 

(c) 

68. Arrange in order of C–H bond energy

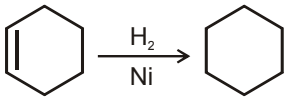


Sol.

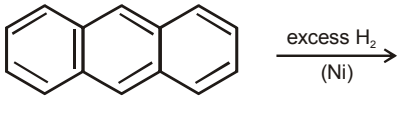
69. How many grams of H_2 released when 46 gm of sodium is treated with excess of ethyl alcohol.

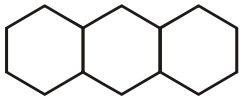
Sol.

70. Use the following data to answer the questions below:



$\Delta H = -28.6$ Kcal mol^{-1}





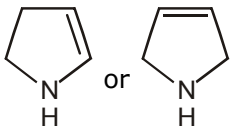
$\Delta H = -116.2$ Kcal mol^{-1}

Anthracene

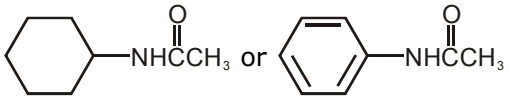
Calculate the resonance energy of anthracene in kcal/mol.

Sol.

71. (A) Which compound has the greater electron density on its nitrogen atom ?



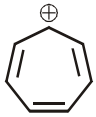
(B) Which coompound has the greater electron density on its oxygen atom ?



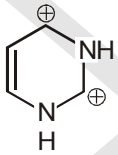
Sol.

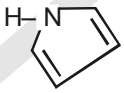
72. Match the column:

Column I

(A) 

(B) 

(C) 

(D) 

Column II

(P) Six π electrons

(Q) Four π electrons

(R) Aromatic Compounds

(S) Anti-aromatic compound

Sol.

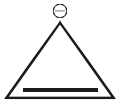
73. Match the column:

Column I

(A) 

(B) 

(C) 

(D) 

Column II

(P) Hybrid state of each atom sp^2

(Q) Anti aromatic

(R) Delocalisation of π bond

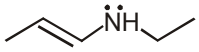
(S) Non aromatic

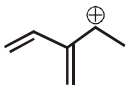
(T) Obeys Huckel's Rule for aromatically

Sol.

74. Match the column:

Column I

(A) 

(B) 

(C) 

(D) 

Column II

(P) Non aromatic

(Q) Anti aromatic

(R) Resonance

(S) Aromatic

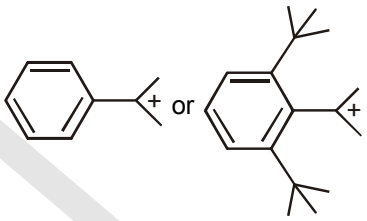
Sol.

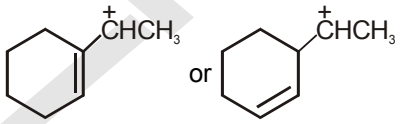
75. Match the column:

Column I

(A) $CH_3O\overset{+}{C}H_2$ or $CH_2NH\overset{+}{C}H_2$

(B) $CH_3OCH_2\overset{+}{C}H_2$ or $CH_3O\overset{+}{C}H_2$

(C) 

(D) 

Column II

(P) First is more stable than second

(Q) Second is more stable than first

(R) Not resonating structure of each other

(S) Resonance is present in both carbocation

Sol.

EXERCISE – III

JEE ADVANCED

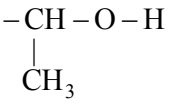
Q.1 Write the correct order of acidic strength of following compounds:

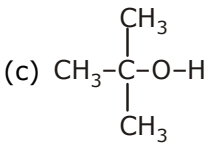
(i) (a) H–F (b) H–Cl (c) H–Br
(d) H–I

Sol.

(ii) (a) CH_4 (b) NH_3 (c) H_2O
(d) H–F

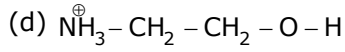
Sol.

(iii) (a) $CH_3–CH_2–O–H$ (b) 

(c) 

Sol.

(iv) (a) $F–CH_2–CH_2–O–H$
(b) $NO_2–CH_2–CH_2–O–H$
(c) $Br–CH_2–CH_2–O–H$

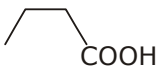
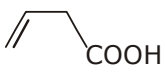
(d) 

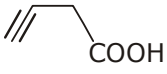
Sol.

Q.2 Write the correct order of acidic strength of following compounds:

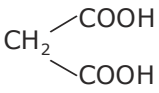
(i) (a) CH_3COOH (b) CH_3CH_2OH
(c) C_6H_5OH (d) $C_6H_5SO_3H$

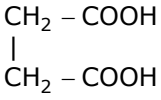
Sol.

(ii) (a)  (b) 

(c) 

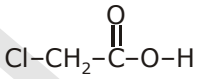
Sol.

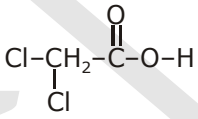
(iii) (a)  (b) 

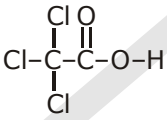
(c) 

Sol.

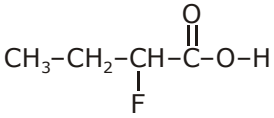
Q.3 Write correct order of acidic strength of following compounds:

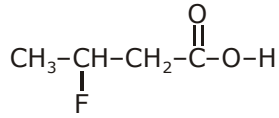
(i) (a) 

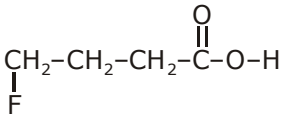
(b) 

(c) 

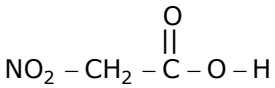
Sol.

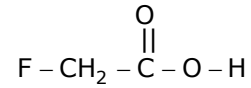
(ii) (a) 

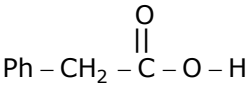
(b) 

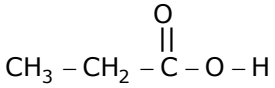
(c) 

Sol.

(iii) (a) 

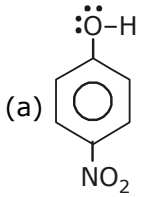
(b) 

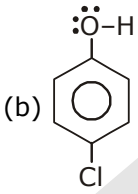
(c) 

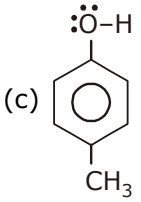
(d) 

Sol.

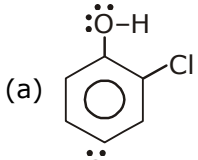
Q.4 Write correct order of acidic strength of following compounds:

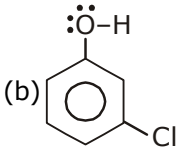
(i) (a) 

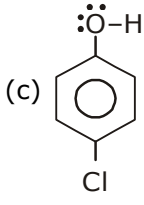
(b) 

(c) 

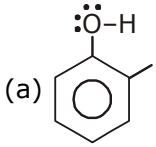
Sol.

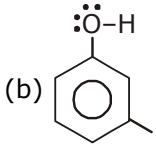
(ii) (a) 

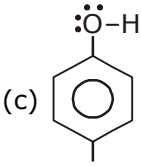
(b) 

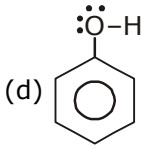
(c) 

Sol.

(iii) (a) 

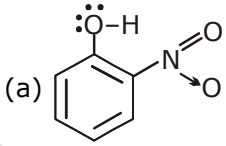
(b) 

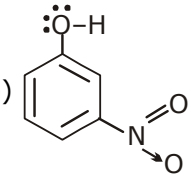
(c) 

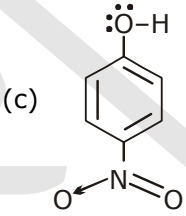
(d) 

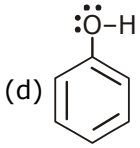
Sol.

Q.5 Write correct order of acidic strength of following compounds:

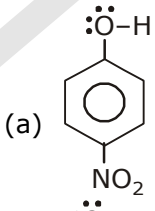
(i) (a) 

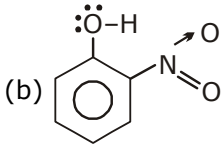
(b) 

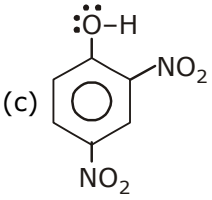
(c) 

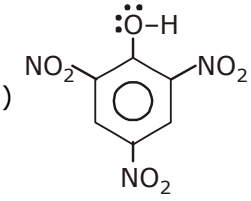
(d) 

Sol.

(ii) (a) 

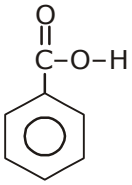
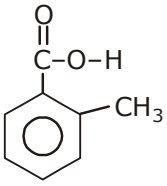
(b) 

(c) 

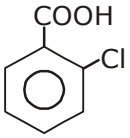
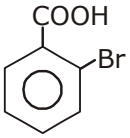
(d) 

Sol.

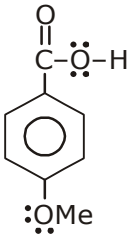
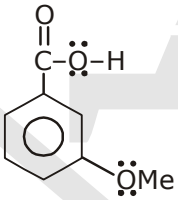
Q.6 Write correct order of acidic strength of following compounds:

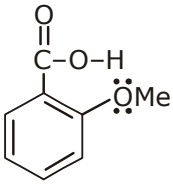
(i) (a)  (b) 

Sol.

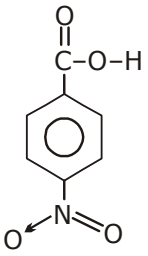
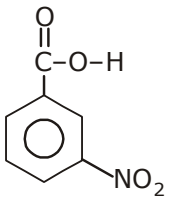
(ii) (a)  (b) 

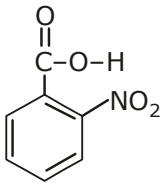
Sol.

(iii) (a)  (b) 

(c) 

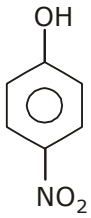
Sol.

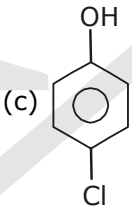
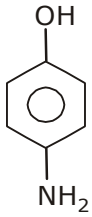
(iv) (a)  (b) 

(c) 

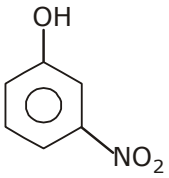
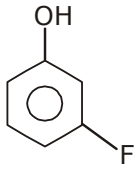
Sol.

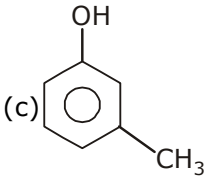
Q.7 Select the strongest acid in each of the following sets :

(i) (a)  (b) 

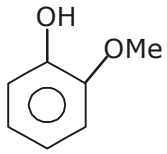
(c)  (d) 

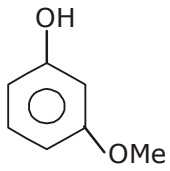
Sol.

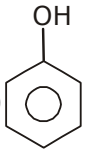
(ii) (a)  (b) 

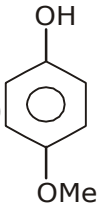
(c)  (d) 

Sol.

(iii) (a) 

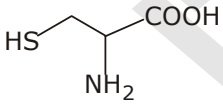
(b) 

(c) 

(d) 

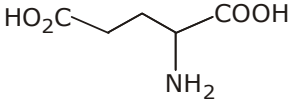
Sol.

Q.8 Say which pk_a belong to which functional group in case of following amino acids :

(i) cysteine : 

1.8, 8.3 & 10.8

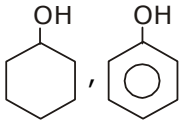
Sol.

(ii) glutamic acid : 

: 2.19, 4.25, 9.67

Sol.

Q.9 Record the following sets of compounds according to increasing pK_a (= – log Ka)

(a) 

, cyclohexane carboxylic acid.

Sol.

(b) 1-butyne, 1-butene, butane

Sol.

(c) Propanoic acid, 3-bromopropanoic acid, 2-nitropropanoic acid

Sol.

(d) Phenol,o-nitrophenol, o-cresol

Sol.

(e) Hexylamine, aniline, methylamine

Sol.

Q.10 Explain which is a stronger acid.

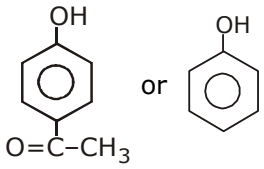
(a) CH_3CH_3 $BrCH_2NO_2$

(b) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ & $CH_3-\overset{O}{\overset{\|}{C}}-CH_2CN$

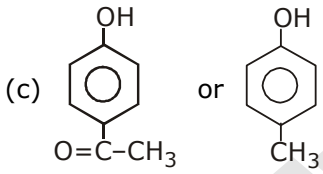
(c) CH_3 – CHO CH_3 – NO_2

Sol.

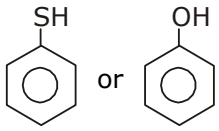
Q.11 Explain which is a weaker acid.

(a)  or

Sol.

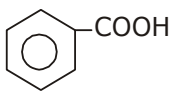
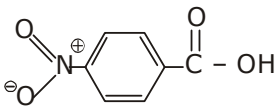
(c) 

Sol.

(b) 

Sol.

Q.12 Which of the following would you predict to be the stronger acid ?

(a)  or 

Sol.

(b) $CH_3 - CH_2 - CH_2 - OH$ or $CH_3 - CH = CH - OH$

Sol.

(c) $CH_3 - CH = CH - CH_2 - OH$ or $CH_3 - CH = CH - OH$

Sol.

Q.13 Write increasing order of basic strength of following:

(i) (a) F^{Θ} (b) Cl^{Θ}

(c) Br^{Θ} (d) I^{Θ}

Sol.

(ii) (a) CH_3^{Θ} (b) NH_2^{Θ}

(c) OH^{Θ} (d) F^{Θ}

Sol.

(iii) (a) $R-NH_2$ (b) $Ph-NH_2$

(c) $R-\underset{\underset{O}{\|}}{C}-NH_2$

Sol.

(iv) (a) NH_3 (b) $MeNH_2$

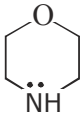
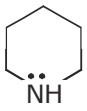
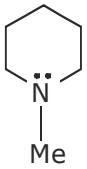
(c) Me_2NH (d) Me_3N (Gas phase)

Sol.

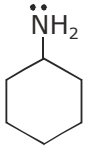
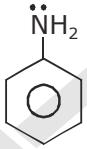
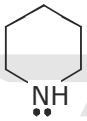
(v) (a) NH_3 (b) $MeNH_2$
(c) Me_2NH (d) Me_3N (in H_2O)

Sol.

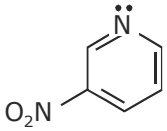
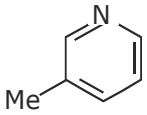
Q.14 Write increasing order of basic strength of following:

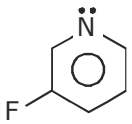
(i) (a)  (b)  (c) 

Sol.

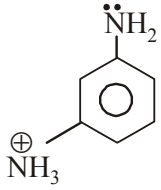
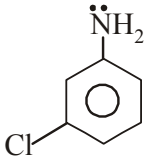
(ii) (a)  (b)  (c) 

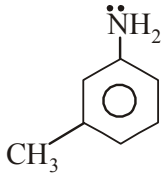
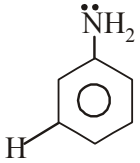
Sol.

(iii) (a)  (b) 

(c) 

Sol.

(iv) (a)  (b) 

(c)  (d) 

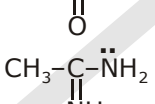
Sol.

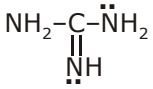
Q.15 Write increasing order of basic strength of following:

(i) (a) $CH_3-CH_2-\ddot{N}H_2$ (b) $CH_3-CH=\ddot{N}H$

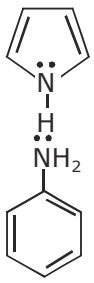
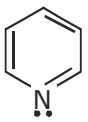
(c) $CH_3-C\equiv\ddot{N}$

Sol.

(ii) (a)  (b) $CH_3-CH_2-\ddot{N}H_2$

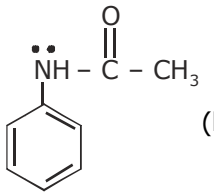
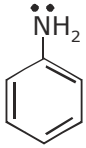
(c) (d) 

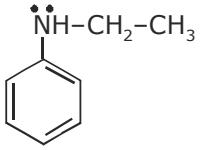
Sol.

(iii) (a)  (b) 

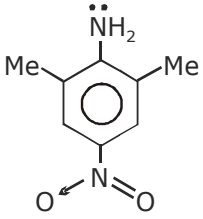
(c)

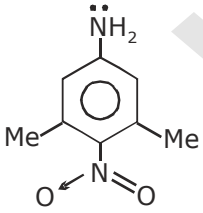
Sol.

(iv) (a)  (b) 

(c) 

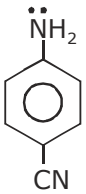
Sol.

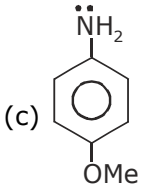
(v) (a) 

(b) 

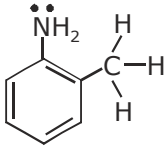
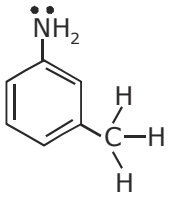
Sol.

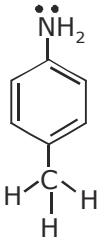
Q.16 Write increasing order of basic strength of following:

(i) (a)  (b) 

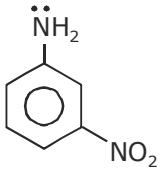
(c)  (d) 

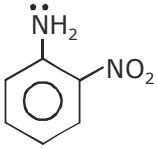
Sol.

(ii) (a  (b) 

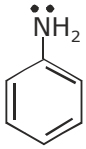
(c) 

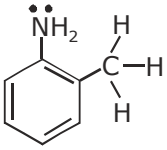
Sol.

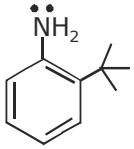
(iii) (a)  (b) 

(c) 

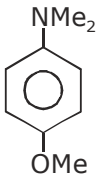
Sol.

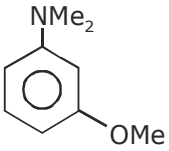
(iv) (a) 

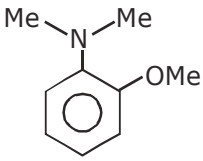
(b) 

(c) 

Sol.

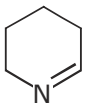
(v) (a) 

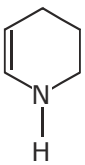
(b) 

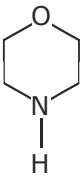
(c) 

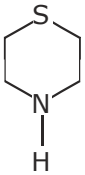
Sol.

Q.17 Select the strongest base in following compound :

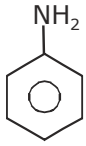
(i) (a) 

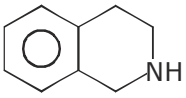
(b) 

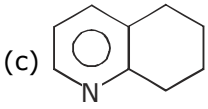
(c) 

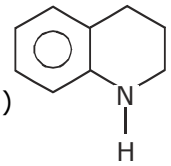
(d) 

Sol.

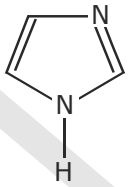
(ii) (a) 

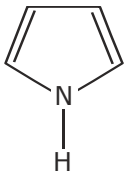
(b) 

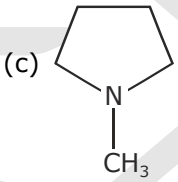
(c) 

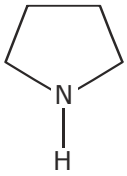
(d) 

Sol.

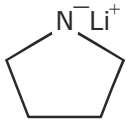
(iii) (a) 

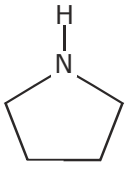
(b) 

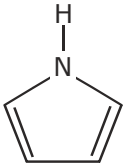
(c) 

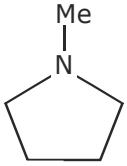
(d) 

Sol.

(iv) (a) 

(b) 

(c) 

(d) 

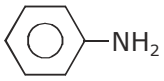
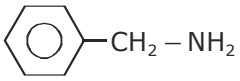
Sol.

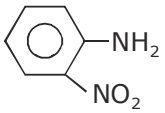
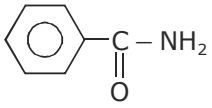
Q.18 Arrange the following compound in decreasing order of their basicity.

(i) (a) $H_2C = CHNa$ (b) CH_3CH_2Na

(c) CH_3CH_2ONa (d) $HC \equiv CNa$

Sol.

(ii) (a)  (b) 

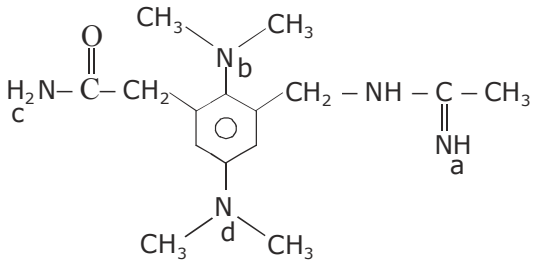
(c)  (d) 

Sol.

(iii) (a) HO^- (b) NH_3 (c) H_2O

Sol.

Q.19 Basicity order in following compound is :



(A) b > d > a > c (B) a > b > d > c

(C) a > b > c > d (D) a > c > b > d

Sol.

Q.20 Consider the following bases:

(I) o-nitroaniline (II) m-nitroaniline

(III) p-nitroaniline

The decreasing order of basicity is:

(A) II > III > I (B) II > I > III

(C) I > II >III (D) I > III > II

Sol.

Q.21 Consider the basicity of the following aromatic amines:

(I) aniline (II) p-nitroaniline

(III) p-methoxyaniline (IV) p-methylaniline

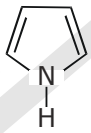
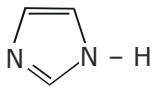
The correct order of decreasing basicity is:

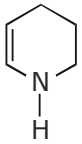
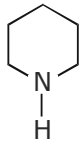
(A) III > IV > I > II (B) III > IV > II > I

(C) I > II > III > IV (D) IV > III > II > I

Sol.

Q.22 Which one of the following is least basic in character?

(A)  (B) 

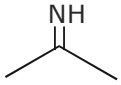
(C)  (D) 

Sol.

Q.23 In each of the following pair of compounds, which is more basic in aqueous solution? Give an explanation for your choice:

(a) CH_3NH_2 or CF_3NH_2

Sol.

(b) CH_3CONH_2 or H_2N  NH_2

Sol.

(c) n-$PrNH_2$ or CH_3CN

Sol.

(d) $C_6H_5N(CH_3)_2$ or 2,6-dimethyl-N-N-dimethylaniline

Sol.

(e) m-nitroaniline or p-nitroaniline

Sol.

Q.24 From the following pair, select the stronger base:

(a) p-methoxy aniline or p-cyanoaniline

Sol.

(b) pyridine or pyrrole

Sol.

(c) CH_3CN or $CH_3CH_2NH_2$

Sol.

Q.25 Choose the member of each of the following pairs of compunds that is likely to be the weaker base.

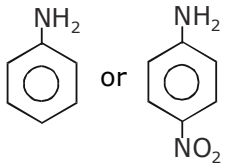
(a) H_2O or $H_3O^{\oplus}$ (b) H_2S, HS^-, S^{2-}

(c) Cl^-, SH^- (d) F^-, OH^-, NH_2^-, CH_3^-

(e) HF, H_2O, NH_3 (f) OH^-, SH^-, SeH^-

Sol.

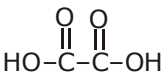
Q.26 Explain which compound is the weaker base.

(a)  or

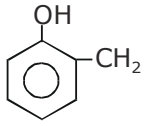
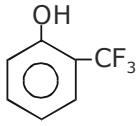
Sol.

(b) $CH_2 = CH - CH = CH - CH_2^-$ or $CH_2 = CH - CH_2^-$

Sol.

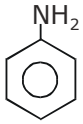
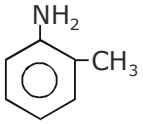
(c)  or 

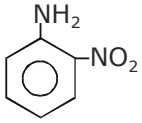
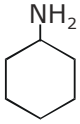
Sol.

(d)  or 

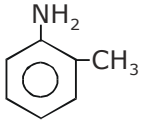
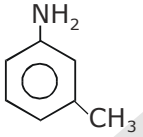
Sol.

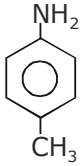
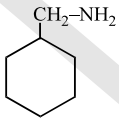
Q.27 Rank the following amines in increasing basic nature.

(a)  (i)  (ii)

 (iii)  (iv)

Sol.

(b)  (i)  (ii)

 (iii)  (iv)

Sol.

Q.28 Arrange the basic strength of the following compounds.

(a) OH^- CH_3COO^- Cl^-

(i) (ii) (iii)

Sol.

(b) $CH \equiv C^-$ $CH_2 = CH^-$ $CH_3CH_2^-$

(i) (ii) (iii)

Sol.

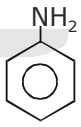
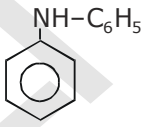
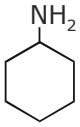
(c) (i) $CH_2 = CHCH_2NH_2$

(ii) $CH_3CH_2CH_2NH_2$

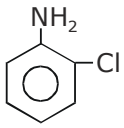
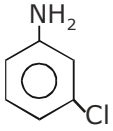
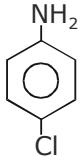
(iii) $CH \equiv C - CH_2NH_2$

Sol.

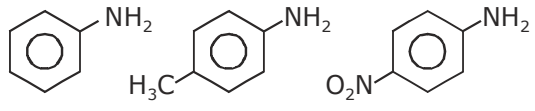
Q.29 Arrange the basic strength of the following compounds.

(a)  (i)  (ii)  (iii)

Sol.

(b)  (i)  (ii)  (iii)

Sol.

(c) 

(i) (ii) (iii)

Sol.

Q.30 Arrange the following compounds in order of increasing basicity.

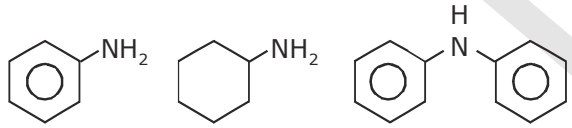
(a) CH_3NH_2, $CH_3\overset{\oplus}{N}H_3$, CH_3NH^-

(b) CH_3O^-, CH_3NH^-, $CH_3CH_2^-$

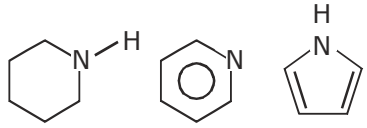
(c) $CH_3CH = CH^-$, $CH_3CH_2CH_2^-$, $CH_3C{\equiv}C^-$

Sol.

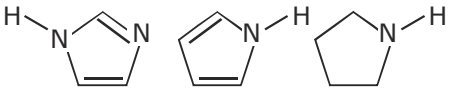
Q.31 Rank the amines in each set in order of increasing basicity.

(a) 

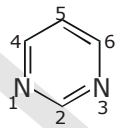
Sol.

(b) 

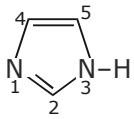
Sol.

(c) 

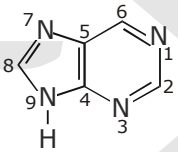
Sol.

Q.32 

Pyrimidine



Imidazole



Purine

Among the following which statement(s) is/are ture:

(A) Both N of pyrimidine are of same basic strength

(B) In imidazole protonation takes places on N–1.

(C) Purine has 3 basic N.

(D) Pyrimidine imidazole and purine all are aromatic

Sol.

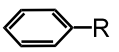
EXERCISE – IV

PREVIOUS YEARS

LEVEL – I

JEE MAIN

Q.1 In the following benzyl/alkyl system

$R - CH = CH_2$ or  (R is alkyl group)

increasing order of inductive effect is – **[AIEEE-2002]**

(A) $(CH_3)_3 C - > (CH_3)_2 CH -> CH_3CH_2—$

(B) $(CH_3CH_2 - > (CH_3)_2 CH -> (CH_3)_3C —$

(C) $(CH_3)_2 CH - > CH_3CH_2 -> (CH_3)_3C—$

(D) $(CH_3)C - > CH_3CH_2 -> (CH_3)_2CH—$

Sol.

Q.2 When – CH_3, $CH_3-\underset{\displaystyle CH_3}{\overset{|}{CH}}-$ & $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{C}}}-$ groups are introduced on benzene ring then correct order of their inductive effect is - **[AIEEE-2002]**

(A) $CH_3 - > CH_3-\underset{\displaystyle CH_3}{\overset{|}{CH}}- > CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{C}}}-$

(B) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{C}}}- > CH_3-\underset{\displaystyle CH_3}{\overset{|}{CH}}- > CH_3 -$

(C) $CH_3-\underset{\displaystyle CH_3}{\overset{|}{CH}}- > CH_3 - > CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{C}}}-$

(D) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{C}}}- > CH_3 - > CH_3-\underset{\displaystyle CH_3}{\overset{|}{CH}}-$

Sol.

Q.3 The correct order of increasing basic no. of the bases NH_3, CH_3NH_2 and $(CH_3)_2NH$ is – **[AIEEE-2003]**

(A) $NH_3 < CH_3NH_2 < (CH_3)_2NH$

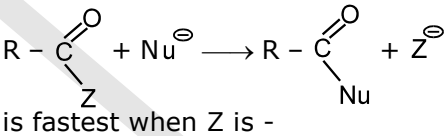
(B) $CH_3NH_2 < (CH_3)_2NH < NH_3$

(C) $CH_3NH_2 < NH_3 < (CH_3)_2NH$

(D) $(CH_3)_2NH < NH_3 < CH_3NH_2$

Sol.

Q.4 Rate of the reaction **[AIEEE-2004]**



is fastest when Z is -

(A) Cl (B) NH_2

(C) OC_2H_5 (D) $OCOCH_3$

Sol.

Q.5 Consider the acidity of the carboxylic acids : **[AIEEE-2004]**

(a) PhCOOH (b) o – $NO_2C_6H_4COOH$

(c) p – $NO_2C_6H_4COOH$ (d) m – $NO_2C_6H_4COOH$

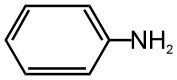
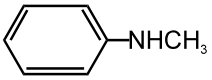
Which of the following order is correct ?

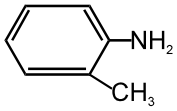
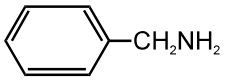
(A) a > b > c > d (B) b > d > c > a

(C) b > d > a > c (D) b > c > d > a

Sol.

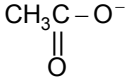
Q.6 Which of the following is the strongest base - **[AIEEE-2004]**

(A)  (B) 

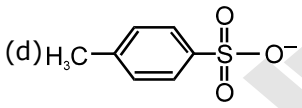
(C)  (D) 

Sol.

Q.7 The decreasing order of nucleophilicity among the nucleophiles **[AIEEE-2005]**

(a)  (b) CH_3O^-

(c) CN^-

(d) 

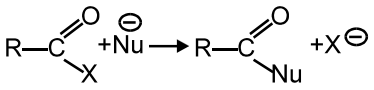
is

(A) (d), (c) , (b) , (a) (B) (a), (b), (c) , (d)

(C) (c) , (b) , (a) , (d) (D) (b), (c) , (a) , (d)

Sol.

Q.8 The reaction **[AIEEE-2005]**



is fastest when X is –

(A) NH_2 (B) Cl

(C) OCOR (D) OC_2H_5

Sol.

Q.9 Amongst the following the most basic compound is– **[AIEEE-2005]**

(A) aniline (B) benzylamine

(C) p–nitroaniline (D) acetanilide

Sol.

Q.10 The increasing order of stability of the following free radicals is – **[AIEEE 2006]**

(A) $(C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$

(B) $(C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C} < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$

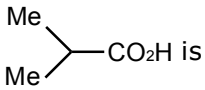
(C) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H$

(D) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C}$

Sol.

Q.11 $CH_3Br + Nu^- \rightarrow CH_3 - Nu + Br^-$
The decreasing order of the rate of the above reaction with nucleophiles (Nu^-) A to D is
[Nu^- = (A) PhO^-, (B) AcO^-, (C) HO^-, (D) CH_3O]
[AIEEE 2006]
(A) D > C > B > A (B) A > B > C > D
(C) B > D > C > A (D) D > C > A > B

Sol.

Q.12 The correct order of increasing acid strength of the compounds **[AIEEE 2006]**
(a) CH_3CO_2H (b) $MeOCH_2CO_2H$
(c) CF_3CO_2H (d)  is
(A) d < a < c < b (B) d < a < b < c
(C) a < d < c < b (D) b < d < a < c

Sol.

Q.13 Which one of the following is the strongest base in aqueous solution ?
[AIEEE-2007]
(A) Trimethylamine (B) Aniline
(C) Dimethylamine (D) Methylamine

Sol.

Q.14 Presence of a nitro group in a benzene ring- **[AIEEE 2007]**
(A) activates the ring towards electrophilic substitution
(B) renders the ring basic
(C) deactivates the ring towards nucleophilic substitution
(D) deactivates the ring towards electrophilic substitution

Sol.

Q.15 Arrange the carbanions, $(CH_3)_3\overline{C}$, $\overline{C}Cl_3$, $(CH_3)_2\overline{C}H$, $C_6H_5\overline{C}H_2$, in order of their decreasing stability- **[AIEEE 2009]**
(A) $(CH_3)_2\overline{C}H > \overline{C}Cl_3 > C_6H_5\overline{C}H_2 > (CH_3)_3\overline{C}$
(B) $\overline{C}Cl_3 > C_6H_5\overline{C}H_2 > (CH_3)_2\overline{C}H > (CH_3)_3\overline{C}$
(C) $(CH_3)_3\overline{C} > (CH_3)_2\overline{C}H > C_6H_5\overline{C}H_2 > \overline{C}Cl_3$
(D) $C_6H_5\overline{C}H_2 > \overline{C}Cl_3 > (CH_3)_3\overline{C} > (CH_3)_2\overline{C}H$

Sol.

Q.16 The correct order of increasing basicity of the given conjugate bases (R = CH_3) is
[AIEEE 2010]
(A) $RCOO^- < HC \equiv C^- < R^- < N^-H$
(B) $R^- < HC \equiv C^- < RCOO^- < N^-H$
(C) $RCOO^- < N^-H < HC \equiv C^- < R^-$
(D) $RCOO^- < HC \equiv C^- < N^-H < R^-$

Sol.

Q.17 The strongest acid amongst the following compounds is : **[AIEEE 2011]**
(A) HCOOH
(B) $CH_3CH_2CH(Cl)COOH$
(C) $ClCH_2CH_2CH_2COOH$
(D) CH_3COOH

Sol.

LEVEL – II

JEE ADVANCED

1. Which of the following hydrocarbons has the lowest dipole moment? **[JEE-2002]**

(A) cis-2-butene (B) 2-butyne

(C) 1-butyne (D) $H_2C = CH - C \equiv CH$

Sol.

2. Which of the following acids has the smallest dissociation constant ? **[JEE-2002]**

(A) $CH_3CHFCOOH$ (B) FCH_2CH_2COOH

(C) $BrCH_2CH_2COOH$ (D) $CH_3CHBrCOOH$

Sol.

3. Which ofthe following represent the given mode of hybridisation $sp^2 - sp^2 - sp - sp$ from left to right ? **[JEE-2003]**

(A) $CH_2 = CH - C \equiv CH$ (B) $HC \equiv C - C \equiv CH$

(C) $H_2C = C = C = CH_2$ (D) 

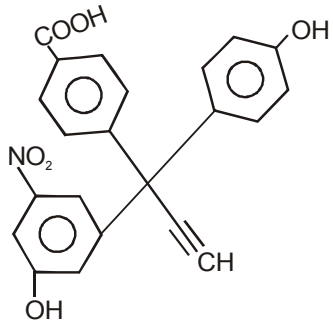
Sol.

4. Maximum dipolemoment will be of **[JEE-2003]**

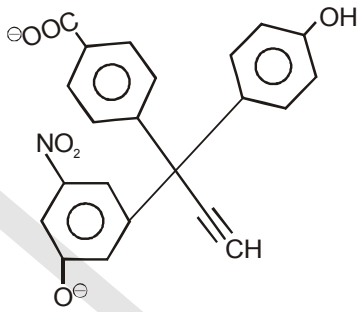
(A) CCl_4 (B) $CHCl_3$

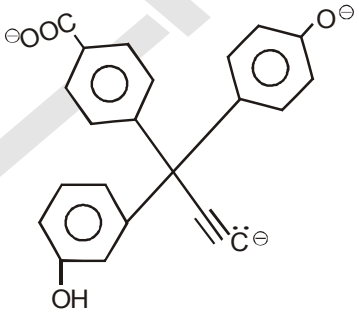
(C) CH_2Cl_2 (D) CH_3Cl

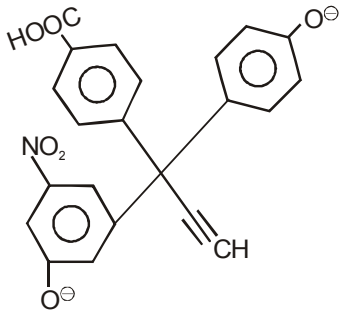
Sol.

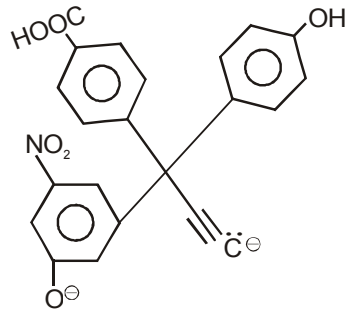
5. 

Product (A). The product A will be **[JEE-2003]**

(A) 

(B) 

(C) 

(D) 

Sol.

6. Out of anhydrous $AlCl_3$ and hydrous $AlCl_3$ which is more soluble in diethyleither ? Explain with reason.

[JEE-2003]

Sol.

7. Match K_a values with suitable acid:

[JEE-2003]

K_a

(i) 3.3×10^{-5}

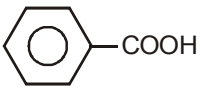
(ii) 4.2×10^{-5}

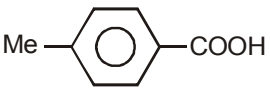
(iii) 6.3×10^{-5}

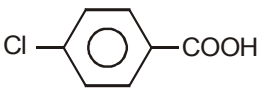
(iv) 6.4×10^{-5}

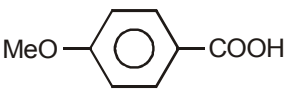
(v) 30.6×10^{-5}

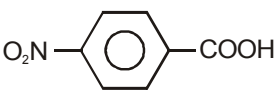
Acid

(A) 

(B) 

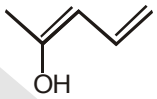
(C) 

(D) 

(E) 

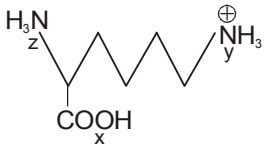
Sol.

8. Give resonating structures of following compound:



[JEE-2003]

Sol.

9.  **[JEE-2004]**

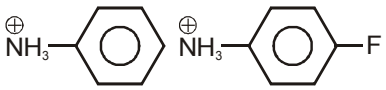
Correct order of acidic strength is

(A) x > y > z (B) z > y > x

(C) y > z > x (D) x > z > y

Sol.

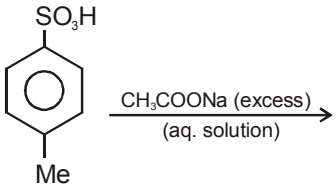
10. Which of the following is more acidic and why ?



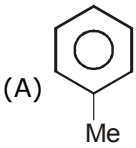
[JEE-2004]

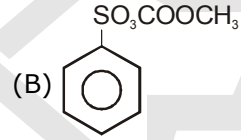
Sol.

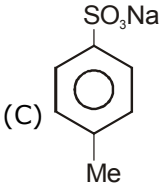
11.

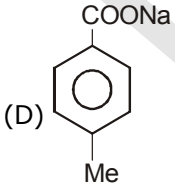


[JEE-2005]

(A) 

(B) 

(C) 

(D) 

$+ H_2SO_3$

Sol.

12. For 1-methoxy-1,3-butadiene, which of the following resonating structure is the least stable ? **[JEE-2005]**

(A) $H_2\overset{\ominus}{C} - \overset{\oplus}{C}H - CH = CH - O - CH_3$

(B) $H_2\overset{\ominus}{C} - CH = CH - CH = \overset{\oplus}{O} - CH_3$

(C) $H_2C = CH = \overset{\oplus}{C}H - \overset{\ominus}{C}H - O - CH_3$

(D) $H_2C = CH - \overset{\ominus}{C}H - CH = \overset{\oplus}{O} - CH_3$

Sol.

13. Predict whether the following molecules are iso structural or not. Justify your answer. **[JEE-2005]**

(i) $NMe_{(3}$ (ii) $N(SiMe_3)_3$

Sol.

14. When benzene sulfonic acid and p-nitrophenol are treated with $NaHCO_3$, the gases released respectively are **[JEE-2006]**

(A) SO_2, NO_2 (B) SO_2,NO

(C) SO_2,CO_2 (D) CO_2,CO_2

Sol.

15. (I) 1, 2-dihydroxy beznene

(II) 1, 3-dihydroxy benzene

(III) 1, 4-dihydroxy benzene

(IV) Hydroxy benzene

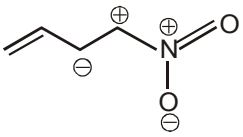
The increasing order of boiling points of above mentioned alcohols is **[JEE-2006]**

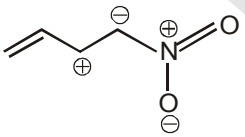
(A) I < II < III < IV (B) I < II < IV < III

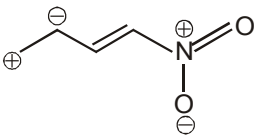
(C) IV < I < II < III (D) IV < II < I < III

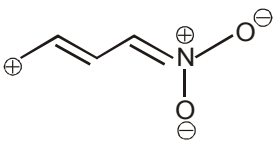
Sol.

16. Among the following, the least stable resonance structur is **[JEE-2007]**

(A) 

(B) 

(C) 

(D) 

Sol.

17. **Statement-1:** p-Hydroxybenzoic acid has a lower boiling point then o-hydroxybenzoic acid.

Statement-2: o-Hydroxybenzoic acid has a intramoleculer hydrogen bonding.

[JEE-2007]

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT correct explanation for statement-1.

(C) Statement1 is true, statement-2 is false.

(D) Statement1 is false, statement-2 is true.

Sol.

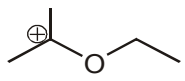
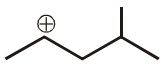
18. Hyperconjugation involves overlap of the following orbitals **[JEE-2008]**

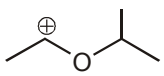
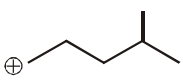
(A) $\sigma - \sigma$ (B) $\sigma - p$

(C) $p - p$ (D) $\pi - \pi$

Sol.

19. The correct stability order for the following species is **[JEE-2008]**

(I)  (II) 

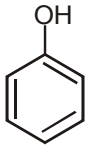
(III)  (IV) 

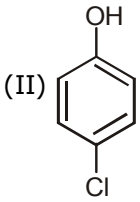
(A) II > IV > I > III (B) I > II > III > IV

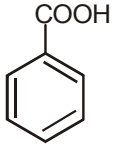
(C) II > I > IV > III (D) I > III > II > IV

Sol.

20. The correct acidity order of the following is **[JEE-2009]**

(I) 

(II) 

(III) 

(IV) 

(A) III > IV > II > I (B) IV > III > I > II
(C) III > II > I > IV (D) II > III > IV > I

Sol.

21. The correct stability order of the following resonance structures is **[JEE-2009]**

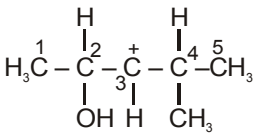
(I) $H_2C = \overset{+}{N} = \overline{N}$ (II) $H_2\overset{+}{C} - N = \overline{N}$

(III) $H_2\overline{C} - \overset{+}{N} = N$ (IV) $H_2\overline{C} - N = \overset{+}{N}$

(A) I > II > IV > III (B) I > III > II > IV
(C) II > I > III > IV (D) III > I > IV > II

Sol.

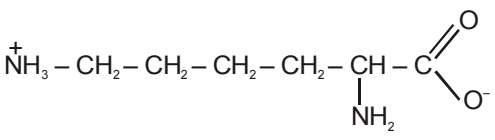
22. In the following carbocation; H/CH_3 that is most likely to migrate to the positively charged carbon is **[JEE-2009]**



(A) CH_3 at C-4 (B) H at C-4
(C) CH_3 at C-2 (D) H at C-2

Sol.

23. The total number of basic group in the following form of lysine is **[JEE-2010]**



Sol.

24. Among the following compounds, the most acidic is: **[JEE-2011]**

(A) p-nitrophenol

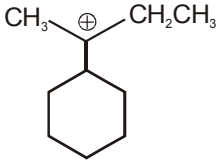
(B) p-hydroxybenzoic acid

(C) o-hydroxybenzoic acid

(D) p-toluic acid

Sol.

25. The total number of contrubting structure showing hyperconjugation (involving C-H bonds) for the following carbocation is



[JEE-2011]

Sol.

26. In Allen (C_3H_4), the type (s) of hybridisation of the carbon atoms is (are)**[JEE-2012]**

(A) sp and sp^3 (B) sp and sp^2

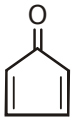
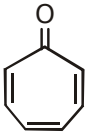
(C) only sp^2 (D) sp^2 and sp^3

Sol.

27. Which of the following molecules in pure from is (are) **unstable** at room temperature

[JEE-2012]

(A)  (B) 

(C)  (D) 

Sol.

Answers

Exercise-I

1. A	**2.** C	**3.** B	**4.** C	**5.** D	**6.** C	**7.** B
8. D	**9.** B	**10.** C	**11.** D	**12.** A	**13.** C	**14.** C
15. D	**16.** A	**17.** C	**18.** B	**19.** C	**20.** B	**21.** C
22. D	**23.** B	**24.** B	**25.** D	**26.** C	**27.** A	**28.** C
29. B	**30.** B	**31.** C	**32.** D	**33.** B	**34.** A	**35.** C
36. A	**37.** D	**38.** C	**39.** B	**40.** B	**41.** A	**42.** A
43. C	**44.** B	**45.** A	**46.** C	**47.** B	**48.** C	**49.** C
50. A	**51.** D	**52.** A	**53.** A	**54.** C	**55.** B	**56.** A
57. D	**58.** D	**59.** B	**60.** D	**61.** B	**62.** C	**63.** B
64. C	**65.** D	**66.** A	**67.** C	**68.** B	**69.** B	**70.** B
71. D	**72.** C	**73.** B	**74.** A	**75.** B	**76.** A	**77.** B
78. D	**79.** C					

Exercise-II

1. A	**2.** C	**3.** C	**4.** A	**5.** B	**6.** B	**7.** C
8. A	**9.** A	**10.** A	**11.** C	**12.** B	**13.** C	**14.** B
15. B	**16.** B	**17.** A	**18.** ABCD	**19.** B,D	**20.** a,b,c,d,f	**21.** c,f
22. b,d,e	**23.** b,d,e	**24.** A,B,D	**25.** A,B,C	**26.** B, E, I	**27.** B, D	

28. a = Resonance form, b = A, c = C, d = A & B, e = B & C, f = 0, g = B, h = B

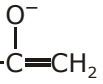
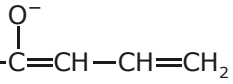
29. (a) is resonance form; (b) is not resonance form due to different number of ℓ.p. and b. p.

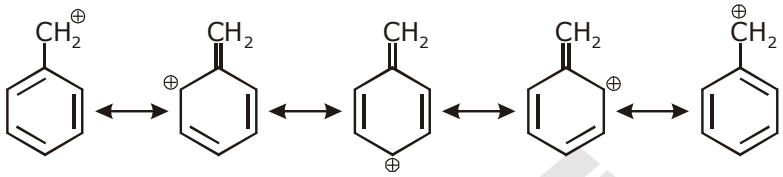
(c) is not resoanance form due to different no. of ℓ.p. and b.p.

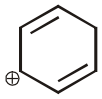
30. (A) sp^2, (B) sp^2, (C) sp^2, (D) sp^2

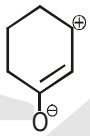
31. $HC \equiv C - C \equiv CH$ in it all carbon are sp hybridized C – C σ-bond is shorter than both CH_3CH_3 & $CH_2=CH-CH=CH$

32. (a) I, (b) I, (c) II, (d) II

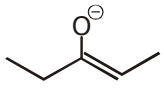
33. (a)  (b) 

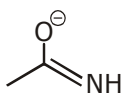
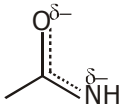
(c) 

(d)  (e) 

(f)  (g)  (h) 

(i) $CH_3-\overset{\oplus}{C}H-CH=CH-CH=CH-CH_3$ (j) $CH_3-\overset{\oplus}{C}H-CH=CH-CH=CH_2$

(k) $H_2\overset{\ominus}{C} - CH = CH - CH = CH_2$ (l)  (m) $Me-CH=\overset{\oplus}{Cl}$

34. (A) $(Me)_2C=\overset{\oplus}{N}H_2$ $(Me)_2\overset{\delta+}{C}\cdots\overset{\delta+}{N}H_2$ (B)  

37. (a) II, (b) II, (c) II, $CH_3 - \overset{O}{\overset{\|}{C}} - CH - CH = \overset{O^{\ominus}}{\overset{|}{C}} - CH_3$ (d) II, $CH_3-CH=CH-CH=\overset{+}{N}\begin{matrix}O^{\ominus}\\ \diagup\\ \diagdown\\ O^{\ominus}\end{matrix}$

(e) II, $CH_3 - CH_2 - \overset{\overset{+}{N}H_2}{\overset{\|}{C}} - NH_2$

38. (a) ii, (b) ii, (c) ii, (d) i, (e) i

39. (a) I, (b) I, (c) I, (d) II, (e) II

40. (a) I, (b) II, (c) II, (d) II, (e) I

41. (a), (c), (d), (g), (j), (l), (m)

42. (a), (b)

43. (a), (b), (c), (f)

44. (a) II, (b) I, (c) I, (d) I, (e) I

45. (a) II, (b) I, (c) I, (d) II

46. (a) II, (b) I, (c) II, (d) II, (e) II

47. (a) II, (b) II, (c) II, (d) II

48. (a) I, (b) II, (c) II, (d) I (e) I

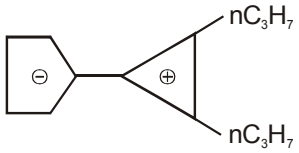
49. (a) II, (b) I, (c) I, (d) I, (e) II

50. (a) I, (b) I, (c) II (d) I (e) I (f) I

51. iii > ii > i

52. (a) ii < Iv < i < iii (b) iii < ii < i

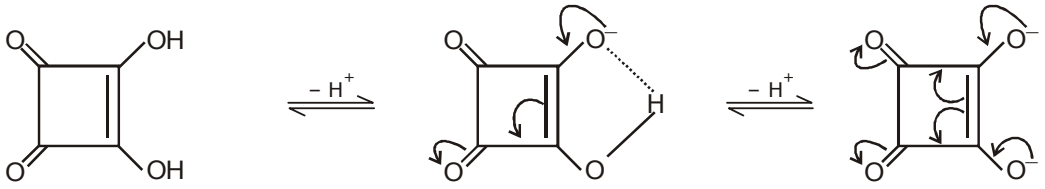
53. (a) A, (b) A, (c) N. A. (d) A, (e) A, (f) N.A. (g) A

54. 

One of the R. S. is having both ring aromatic.

55. A > B

56.



R-stablized & intra H-bonding 4 Eq. R.S.

57. (a) 4658, (b) 4638, (c) 4632, (d) 4656 (e) 5293

58. (a) i, (b) i, (c) ii

59. A

60. (a) (i) D > C > B > A (ii) E > C > D > B > A (b) 2 > 1 (c) 2 < 1 (d) 1 < 2 (e) 1 > 2

61. (A) (I) iv > iii > ii > i, (II) i > ii > iii > iv

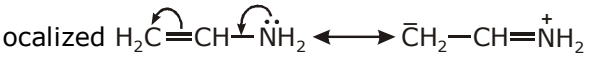
(B) (I) iii > ii > i (II) i > ii > iii

62. (a) I, (b) I, (c) II, (d) I

63. (a) Due to resonance 

(b) In $CH_2=CH-OCH_3$, there is single bond character due to resonance

(c) Conjugate base of CH_3SH ie, $CH_3\bar{S}$ is more stable than conjugate base of CH_3OH, ie CH_3O^-

(d) In $CH_2=CH-NH_2$ lone pair of N is delocalized 

64. (i) c > b > a (ii) c > b > a (iii) b > c > a (iv) c > b > a

(v) c > b > a (vi) b > c > a (vii) a > b > c (viii) a > b > c

(ix) a > c > b (x) d > c > b > a (xi) a > b > c (xii) c > b > a

65. (i) b > c > a (ii) b > c > a > d (iii) c > a > b (iv) a < b

(v) a > b (vi) a > b > c (vii) a > b > c (viii) a > b > c

(ix) a > b (x) c > b > a > d (xi) a > c > b (xii) c > a > b

(xiii) a > b > c > d

66. (i) b > a (ii) a > b > d > c (iii) a > b > c > d > e (iv) b > c > a

(v) a > b > c (vi) a > b > c (vii) b > a (viii) b > a

67. (i) c > b > a (ii) a > b > c > d (iii) a > b (iv) c > b > a

68. d < f < b < c < a < e

On the basis of stability of free radical formed after removal of $H\odot$.

69. $2\ C_2H_5OH + 2Na\ (46g) \rightarrow 2\ C_2H_5ONa + H_2$

$\frac{46}{23} \Rightarrow$ 2 mole Na $\longrightarrow$ 1 mole H_2 generate

It means 2g H_2 gas

70. Anthracene is 14 π e's system

i.e. there are 7 π bonds

Expected (theoretical) heat of hydrogen = – 28.6×7 = – 200.2 kcal/mol

Observed (experimental) heat of hydrogen = –116.2

$\therefore$ R. E. = – 166.2 – (–200.2)

= 84 kcal/mol

71. (A) Second ; (B) First

72. (A) P, R; (B) Q, S; (c) P, R; (D) P, R

73. (A) P, R, T; (B) P, R, S (C) S ; (D) P, Q, R

74. (A) P, R; (B) P, R; (C) R, S; (D) P, R

75. (A) Q, R, S; (B) Q, R; (C) P, R; (D) P, R

Exercise-III

Q.1 (i) d > c > b > a (ii) d > c > b > a (iii) a > b > c (iv) d > b > a > c

Q.2 (i) d > a > c> b (ii) c > b > a (iii) a > b > c

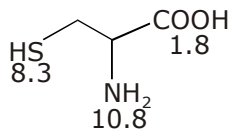
Q.3 (i) c > b > a (ii) a > b > c (iii) a > b > c > d

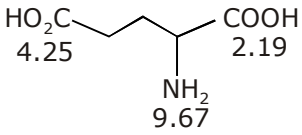
Q.4 (i) a > b > c (ii) a > b > c (iii) d > b > c > a

Q.5 (i) c > a > b > d (ii) d > c > a > b

Q.6 (i) b > a (ii) b > a (iii) c > b > a (iv) c > a > b

Q.7 (i) b (ii) a (iii) b

Q.8 (i) cysteine : 

(ii) glutamic acid : 

Q.9 (a) 3 < 2 < 1; (b) 1 < 2 < 3; (c) 3 < 2 < 1; (d) 2 < 1 < 3; (e) 2 < 3 < 1

Q.10 (a) 2; (b) 2; (c) 2 **Q.**11 (a) 2; (b) 2; (c) 2 **Q.**12 (a) 2; (b) 2; (c) 2

Q.13 (i) a > b > c > d (ii) a > b > c> d (iii) a > b > c (iv) a < b < c < d
(v) c > b> d> a

Q.14 (i) a < b < c (ii) c > a > b (iii) b > c > a (iv) c > d > b > a

Q.15 (i) a > b > c (ii) d > c > b > a (iii) b > c > a (iv) c > b > a (v) b > a

Q.16 (i) d > c > b > a (ii) c > b > a (iii) b > a > c (iv) a > b > c (v) c > a > b

Q.17 (i) d (ii) b (iii) a (iv) a **Q.**18 (i) b > a > d > c (ii) b > a > c > d (iii) a > b > c

Q.19 B **Q.**20 A **Q.**21 A **Q.**22 A

Q.23 (a) i, (b) ii, (c) i, (d) ii, (e) i **Q.**24 (a) i, (b) i, (c) ii

Q.25 (a) 2; (b) 1; (c) 1; (d) 1; (e) 1; (f) 3 **Q.**26 (a) 2; (b) 1; (c) 2; (d) 2

Q.27 (a) 3 < 2 < 1 < 4; (b) 1 < 2 < 3 < 4 **Q.**28 (a) 1 > 2 > 3; (b) 1 < 2 < 3; (c) 3 < 1 < 2

Q.29 (a) 2 < 1 < 3; (b) 1 < 2 < 3; (c) 2 > 1 > 3 **Q.**30 (a) 2 < 1 < 3; (b) 1 < 2 < 3; (c) 3 < 1 < 2

Q.31 (a) 2 > 1> 3, (b) 1 > 2 > 3, (c) 1 > 3 > 2, **Q.**32 A, B, C, D

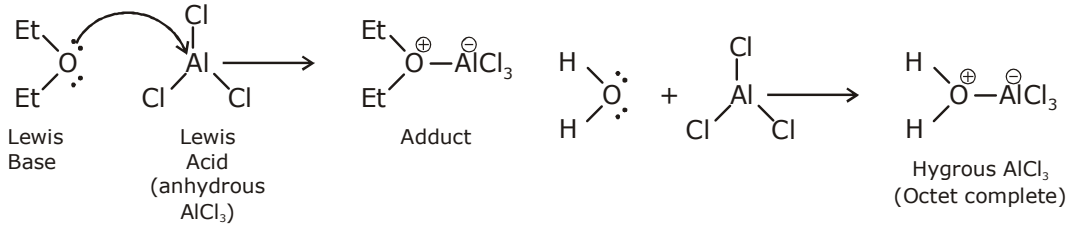
Exercise-IV

LEVEL-1

LEVEL-2

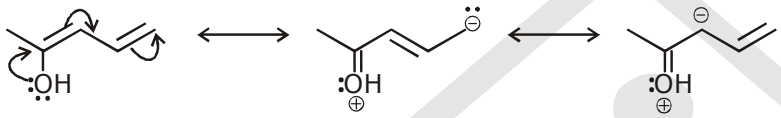
1. B **2.** C **3.** A **4.** D **5.** A

6. Anhydroush $AlCl_3$ is more soluble in diethyl ether



7. (i) d (ii) b (iii) a (iv) c (v) e

8.



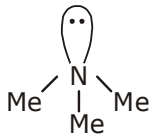
9. D **10.**

is more acidi than

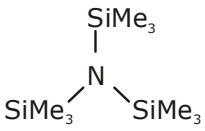
due to –I effect of fluorine.

11. C **12.** C

13.



(Pyramidical)



Given componds are not isostrucutral

Delocalised of l.p. of nitrogen in vacant d-orbital of silicon makes compound planar.

14. D **15.** C **16.** A **17.** D **18.** B **19.** D **20.** A **21.** B

22. D **23.** 2 **24.** C **25.** 6 **26.** B **27.** B

OXIDATION & REDUCTION

OXIDATION REDUCTION

Oxidation is the process involving addition of oxygen or removal of hydrogen or both.

Examples of oxidation:

$Fe \longrightarrow FeO$ (Addition of oxygen)

$CH_3CH_2OH \longrightarrow CH_3CHO$ (removal of hydrogen)

$CH_3CH_2OH \longrightarrow CH_3COOH$ (both)

Reduction is just the reverse process. It involves addition of hydrogen or removal of oxygen or both.

Examples of reduction:

$ZnO \longrightarrow Zn$ (removal of oxygen)

$C_2H_4 \longrightarrow C_2H_6$ (addition of hydrogen)

$CH_3COOH \longrightarrow CH_3CH_2OH$ (both)

Limitations of old concept:

(i) It includes only the reactions involving oxygen and hydrogen atoms: For example:

$Fe \longrightarrow FeO$ and $Fe \longrightarrow FeCl_2$

Both the processes are similar because in both the processes, iron is forming a compound from its elemental state, in which its valency is two. The first process is oxidation but second process is not oxidation by this definition, because it does not involve oxygen or hydrogen atoms.

(ii) There may be some process even involving oxygen and hydrogen atoms, which cannot be classified as oxidation or reduction. For example:

$Fe \longrightarrow FeCl_2$ (Oxidation, addition of Cl atoms)

$CH_2=CH_2 \longrightarrow \underset{\underset{OH}{|}}{CH_2}-\underset{\underset{OH}{|}}{CH_2}$ (Oxidation, addition of –OH groups)

The process involves addition of oxygen as well as hydrogen and hence it cannot be classified as oxidation reduction by this definition.

(iii) Conversion of sodium into sodium hydride is oxidation process, but it is reduction by this definition.

$Na \longrightarrow NaH$ (addition of hydrogen)

Modification:

The old definition may be modified by replacing oxygen atom with electronegative atom or group and replacing hydrogen atom with electropositive atom or group.

$Fe \longrightarrow FeCl_2$ (Oxidation, addition of Cl atoms)

$CH_2=CH_2 \longrightarrow \underset{\underset{OH}{|}}{CH_2}-\underset{\underset{OH}{|}}{CH_2}$ (Oxidation, addition of –OH group)

MODERN CONCEPT

(1) In terms of electrons:

Oxidation is the process involving loss of electrons and reduction is the process involving gain of electrons.

Examples:

$Zn \longrightarrow Zn^{2+}+2e$ (Oxidation)

$2Cl^- \longrightarrow Cl_2+2e$ (Oxidation)

$Cu^{2+}+2e \longrightarrow Cu$ (Reduction)

$MnO_4^-+8H^++5e \longrightarrow Mn^{2+}+4H_2O$ (Reduction)

$Cl_2+12\,OH^- \longrightarrow 2ClO_3-+6H_2O+10e$ (Oxidation)

The number of electrons lost or gained can be determined by first conserving the atoms and then, conserving the charge.

2. In terms of oxidation state:

Oxidation is the process involving increase in oxidation state of one or more element while reduction is the process involving decrease in oxidation state of one or more element while reduction is the process involving decrease in oxidation state of one or more element. Oxidation state of any atom in any molecule or ion may be defined as arbitrary charge assigned to that atom according to some well defined rules.

RULES FOR DETERMINATION OF OXID ATION STATE

If the bonded atoms are of element, distribute the shared electron equally between them and if the bonded atoms are different, count shared electron pair for more electronegative atom. Determine the net charge developed on the atoms after re-distribution of shared electrons. It will represent the oxidation states of the atoms. Examples

(i) HCL molecule:

1p 17p

H — Cl

Electrons except shared electrons	0c		16e
Shared electron		2e	
Electron redistribution			2e
Net charge	+1		−1

Hence, O.S. Of H=+1
O.S of Cl = −1

(ii) Cl_2 molecule

17p 17p

Cl — Cl

Electrons except shared electrons	16c		16e
Shared electron		2e	
Electron redistribution	1e		2e
Net charge	0		0

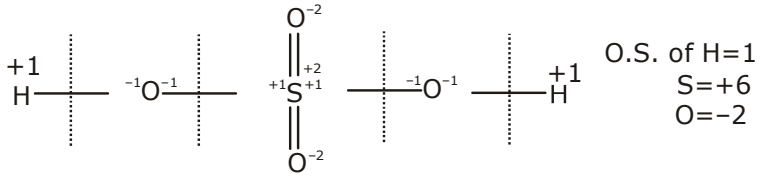
Hence, O.S. Of Cl=0

(iii) H_2O_2 molecule

+1 −1−1 +1
H−O−O−H

The re-distribution of electron may be made simply by assuming the covalent the covalent bonds,, ionic and assigning the charge on atoms on the basis of electronegativities and bond order.

(v) H_2SO_4 molecule



MATHEMATICAL METHOD FOR DETERMINATION OF OXIDATION STATE

Rules I: The oxidation state of any atom is its elemental state is zero.

Rules II: The maximum oxidation state of any atom will be equal to (+group number) and minimum oxidation state will be equal to (group number –8), where group numbers are in roman numerals. For example, Sulphur (S) is member of group VI A and hence its maximum oxidation state is +6 and minimum is (6–8)=–2

Exception: Cu(IB) : +1, +2
Au (IB) : 1, +3
Xe (0) : +2, +4, +6, +8. etc

Rule III: The sum of oxidation state of all the atoms in a molecule is zero and for ions, it is equal to the ionic charge.

Rule IV: The oxidation states of some elements are fixed in all their compounds.

+1: Alkali metals (Li, Na, K, Rb, Cs, Fr) and Ag

+2: Alkaline earth metals (Be. Mg, Ca, Sr, Ba, Ra) and Zn

+3: Al

–1 :F

Rule V: Oxidation state of hydrogen is +1 in all of its compounds, except the metal hydrides, where it –1.

Rule VI: Oxidation state oxygen is –2 in all of compounds except

(i) Peroxide like Na_2O_2, H_2O_2, BaO_2, etc, where it is –1.

(ii) Superoxides like KO_2, RbO_2, etc, where it is 1/2.

(iii) Some other binary compounds of alkali metals and oxygen like KO_3 (O.S. of O=1/3), Rb_2O_3 (O.S. of O=–2/3), etc

(iv) Oxides of fluorine, where it is positive states. For example: O.S. of O in OF_2, O_2F_2,O_3F_2, etc are +2, +1, +2/3, respectively.

Rule VII: The charges on different ions commonly used, should be known.

CO_3^{2-}	Carbonate ion	HCO_3^-	Hydrogen carbonate ion
SiO_4^{4-}	Silicate ion	PO_4^{3-}	Phosphate ion
HPO_4^{2-}	Hydrogen phosphate ion	$H_2PO_4^-$	Dihydrogen phosphate ion
HPO_3^{2-}	Phosphite ion	NO_3^-	Nitrate ion
NO_2^-	Nitrite ion	SO_4^{2-}	Sulphate ion
SO_3^{2-}	Sulphite ion	S^{2-}	Sulphide ion
S_2^{2-}	Pyrite ion	$S_2O_7^{2-}$	Disulphate ion
$S_2O_3^{2-}$	Thiosulphate ion	$S_2O_8^{2-}$	Peroxodisulphate ion
ClO^-	Hypochlorite ion	ClO_3^-	Chlorate ion
ClO_2^-	Chlorite ion	ClO_4^-	Perchlorate ion

Rule VIII: In the complex compound, the overall charge on ligand should be considered in place of considering the charges on individual atoms.

Neutral ligands: H_2O, NH_3, CO, NO, pyridine (Py), ethylenediamine (en), triphenylphoshine (Ph_3P), etc

Negative ligands: X^-, OH^-, NH_2^-, NO_3^-, $C_2O_4^{2-}$, (ox), O^{2-}, O_2^{2-}, SO_4^{2-}, $S_2O_3^{2-}$, CNO^-, etc

Positive ligands: $\overset{+}{N}O$, $\overset{+}{N}O_2$, etc.

Example 1: Determine oxidation state of the underlined atoms in the following compounds or ions.

(A) $\underline{C}H_3^{\oplus}$, $x+3(+1)=+1$, $\therefore x=-2$

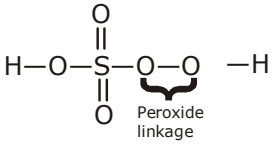
(B) $H_2\underline{S}O_4$, $2(+1)+x+4(-2)=0$, $\therefore x=+6$

(C) $K_2\underline{Cr}_2O_7$, $2(+1)+2x+7(-2)=0$, $\therefore x=+6$

(D) $\underline{Mg}_2\underline{P}_2O_7$, $2(+2)+(-2)=0$, $\therefore x=+5$

(e) $H_2\underline{S}O_5$, $2(+1)+x+5(-2)=0$, $\therefore x=+10$ (not possible)

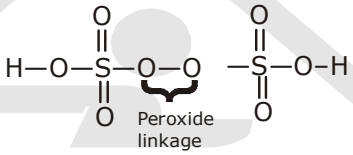
The O.S of S may be up to +6 only. Let us see the structural formula of this compound:



The molecule is containing 3 oxygen atoms in –2 state and 2 in –1 state. Hence, $2(+1)+x+3(-2)+2(-1)=0$, $\therefore x=+6$

(f) $H_2\underline{S}_2O_8$, $2(+1)+2x8(-2)=0$, $\therefore x=+7$ (not possible)

The O.S. of S may be upto +6 only. Let us see the structural formula of this compound:



The molecule is containing 6 oxygen atoms in –2 state and 2 in –1 state. Hence, $2(+1)+2x+6(-2)+2(-1)=0$, $\therefore x=+6$

(g) $\underline{Pb}(\underline{Br}O_3)_2$, Pb and Br, both exhibits variable O.S. As the anion is BrO_3^-ion, the O.S. of Pb may be determined as $x+2(-1)=0$, $x=+2$, and the O.S. of Br may be determined as $y+3(-2)=-1$, $\therefore y=+5$

(h) $\underline{As}_2S_3$, As and S, both exhibits variable O.S. As the binary compounds of sulphur are called sulphides, O.S. fo S=2 Now, for arsenic, $2x+3(-2)=0$, $\therefore x=+3$

(i) $K_4[\underline{Fe}(CN)_6]$, CN^- is negative ligand, $4(+1)+x+6(-1)=0$, $x=+2$

(j) $Ni(CO)_4$, CO is a neutral ligand, $x+4\times0=0$, $x=0$

Example : Classify the following process as oxidation or reducton:

(a)	**Process**	**Answer**
	$Zn \longrightarrow Zn^{2+}$	$\overset{0}{Z}n \longrightarrow Zn^{2+}$
		Increase in O.S., hence **Oxidation**
(b)	$Cl_2 \longrightarrow ClO_3^-$	$\overset{0}{Cl}_2 \longrightarrow \overset{+5}{Cl}O_3^-$

Increase in O.S., hence **Oxidation**

(c) $Cr_2O_7^{2-} \longrightarrow Cr^{3+}$ $\quad \overset{+6}{Cr}_2 O_7^{2-} \longrightarrow Cr^{3+}$

Decrease in O.S., hence **Reduction**

(d) $NO_3^- \longrightarrow NH_4^+$ $\quad \overset{+5}{N} O_3^- \longrightarrow \overset{-3}{N} H_4^+$

Decrease in O.S., hence **Reduction**

TYPE OF REACTIONS

(1) REDOX REACTIONS:

These are the reactions involving oxidation as well as reduction. Examples:

(i) $\overset{0}{Z}n + 2\overset{+1}{H}Cl \longrightarrow \overset{+2}{Z}nCl_2 + \overset{0}{H}_2$

(Oxidation: Zn, Reduction=HCl)

(ii) $K\overset{+7}{M}nO_4 + H_2SO_4 + H_2\overset{-2}{S} \longrightarrow K_2SO_4 + \overset{+2}{M}nSO_4 + H_2O + \overset{0}{S}$

(Oxidation: H_2S, reduction= $KMnO_4$)

Disproportionation reaction:

The redox reaction in which the atoms of same element belonging from the same molecule or ion are oxidised as well as reduced are called disproportionation reaction. Such reaction are also called autoredox on self-redox reaction. Examples:

(i) $3\overset{0}{C}l_2 + 6NaOH \longrightarrow 5NaCl + Na\overset{-1}{C}l + Na\overset{+5}{C}lO_3 + 3H_2O$

Cl–atoms are oxiidised and reduced, both

(ii) $\overset{+4}{M}nO_2 \longrightarrow \overset{+7}{M}nO_4^- + Mn^{2+}$

Mn- atoms are oxidised and reduced, both

(iii) $\overset{-3}{N}H_4\ \overset{+3}{N}O_3 \longrightarrow \overset{0}{N}_2 + 2H_2O$

N—atoms are oxidised and reduced, both, But it is not disproportionation because both N–atoms are belonging from different ions.

Comproportionation reaction

These are just the reverse of disportionation. Atoms of the same element, belonging to the same molecule or ion, oxidise and reduce to give the element in the commom oxidation state. Example:

(i) $2H_2\overset{-2}{S} + \overset{+4}{S}O_2 \longrightarrow \overset{0}{S} + 2H_2O$

(ii) $\overset{+7}{M}nO_4^- + Mn^{2+} \longrightarrow \overset{+4}{M}nO_2$

(iii) $\overset{-3}{N}H_4\ \overset{+3}{N}O_2 \longrightarrow \overset{0}{N}_2 + 2H_2O$

(2) NON-REDOX REACTIONS:

These are the reactions in which neither oxidation nor reduction takes place. Examples:

NEUTRALIZATION REACTIONS

(i) All neutralization (Acid – Base) reactions are non-redox.

$NaOH + HCl \longrightarrow NaCl + H_2O$

$2KOH + H_2SO_4 \longrightarrow K_2SO_4 + 2H_2O$

PRECIPITATION REACTIONS

(ii) Almost all precipitation reactions are non-redox.

$AgNO_3 + NaCl \longrightarrow AgCl\downarrow + NaNO_3$

$Na_2SO_4 + BaCl_2 \longrightarrow BaSO_4\downarrow 2\,NaCl$

Note:- Few precipitation reactions may be redox reaction also

e.g. $CuSO_4 + Zn \longrightarrow Cu\downarrow + ZnSO_4$

$FeO.Cr_2O_3 + Na_2CO_3 + O_2 \longrightarrow Fe_2O_3\downarrow + Na_2CrO_4 + CO_2$

OXIDISING AND REDUCING AGENTS

(1) OXIDISING AGENT:

The substances which oxidises the other substance and themselves undergo reduction in the reaction are called oxidising agents. Most commonly used oxidising agent are $KMnO_4$,$K_2Cr_2O_7$,O_3,I_2, conc. H_2SO_4, conc. HNO_3, etc.

$$2K\overset{+7}{M}nO_4 + 3H_2SO_4 + 10H\overset{-1}{Cl} \longrightarrow K_2SO_4 + 2\overset{+2}{M}nSO_4 + 8H_2O + 5\overset{0}{C}l_2$$

$$\overset{0}{M}g + 2H_2S\overset{+6}{O}_4 \longrightarrow \overset{+2}{M}gSO_4 + \overset{+4}{S}O_2 + 2H_2O$$

Common oxidising agents and their reduced forms in the reactions:

MnO_4^-	$\longrightarrow$	Mn^{2+}	(in acidic medium)
MnO_4^-	$\longrightarrow$	MnO_2	(in neutral of weak basic medium)
MnO_4^-	$\longrightarrow$	MnO_4^{2-}	(in strong basic medium)
$Cr_2O_7^{2-}$	$\longrightarrow$	Cr^{3+}	(in acidic or basic medium)
HNO_3	$\longrightarrow$	NO_2, NO, N_2O, NH_4^+ or H_2	
O_3	$\longrightarrow$	O_2	
F_2	$\longrightarrow$	F^-	
H_2SO_4	$\longrightarrow$	SO_2 or H_2	

2. REDUCING AGENT:

The substances which reduce the other substance and themselves undergo oxidation in the reactions are called reducing agents. Most commonly used reducing agents are metals, HI, H_2S, $LiAlH_4$, $Na_2S_2O_3$, etc.

$$2Na_2\overset{+2}{S}_2O_3 + \overset{0}{I}_2 \longrightarrow Na_2\overset{+2.5}{S}_4O_6 + 2N\overset{-1}{a}l$$

R.A.

$$2H_2\overset{-2}{S} + \overset{+4}{S}O_2 \longrightarrow 3\overset{0}{S} + 2H_2O$$

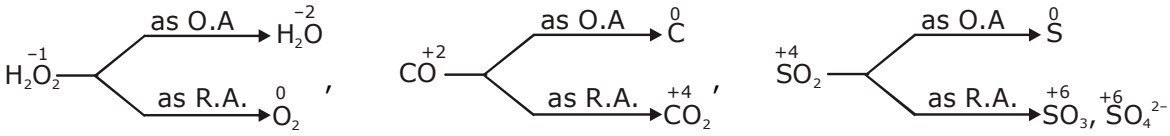
R.A.

Common reducing agents and their oxidised form in the reaction:

$S_2O_3^{2-}$	$\longrightarrow$	$S_4O_6^{2-}$	or SO_4^{2-}
	(with I_2)		(with Cl_2 or Br_2)
I^-	$\longrightarrow$	I_2	
H_2S	$\longrightarrow$	S	
S	$\longrightarrow$	SO_2	

3. Substances in which the central atom is neither in minmum nor in maximum oxidation state can behave as oxidising and reducing agent, both. Some examples are

4. The strength of oxidising and reducing agents depends on a large number of factos like, ionisation energy, electron affinity, hydration energy, etc. Normally, the oxidising powers of elements increases in a period, from left to right and decreases in a group, from top to bottom. The reducing powers of elements have the reverse trend.



SOME IMPORTANT CHEMICAL REACTION

There are some chemical reactions, which a student should remember in order to solve problems on stoichiomertry. These are categorised as

1 COMBINATION OF ELEMENTS WITH OXYGEN

(i) Heating mercury at its boiling point in ari.

$Hg + O_2 \longrightarrow 2HgO$ (red mercuric oxide)

(ii) Heating magnesium in ari. It forms mostly magnesium oxide and some magnesium nitride.

$2Mg+O_2 \longrightarrow 2MgO$

$3Mg + N_2 \longrightarrow Mg_3N_2$

(iii) Calcium behaves similarly.

$2Ca+O_2 \longrightarrow 2CaO$

$3Ca+N_2 \longrightarrow Ca_3N_2$

(iv) Silver does not combin with oxygen, as Ag_2O is unstable to heat.

(v) Many non-metals burn in O_2 forming their respective oxides.

$2H_2+O_2 \longrightarrow 2H_2O$; $S+O_2 \longrightarrow SO_2$

$C+O_2 \longrightarrow CO_2$; $P_4+5O_2 \longrightarrow P_4O_{10}$

$N_2+O_2 \underset{}{\overset{3000°C}{\rightleftharpoons}} 2NO$

Cl_2, Br_2 and I_2 do not directly combine with oxygen.

2. ACTION OF HEAT ON CERTAIN OF OXIDES:

(i) Mercuric oxide and silver oxide are unstable to heat and decompose readily.

$2HgO \xrightarrow{\Delta} 2Hg+O_2$; $2Ag_2O \xrightarrow{\Delta} 4Ag+O_2$

(ii) Various higher oxides, dioxides, mixed oxides and peroxies are decomposed to oxygen and a lower oxide.

$2Pb_3O \longrightarrow 6PbO+O_2$; $2PbO_2 \longrightarrow 2PbO+O_2$

$3MnO_2 \longrightarrow Mn_3O_4+O_2$; $2BaO_2 \longrightarrow 2BaO+O_2$

3. COMPOUNDS RICH IN OXYGEN DECOMPOSE TO GIVE OXYGEN

(i) $2KNO_3 \longrightarrow 2KNO_2+O_2\uparrow$

(ii) $2KMnO_4 \longrightarrow K_2MnO_4+MnO_2+O_2\uparrow$

(purple) (green) (black)

(iii) $4K_2Cr_2O_7 \longrightarrow 4K_2CrO_4+2Cr_2O_3+3O_2\uparrow$

(orange-red) (yellow) (green)

Potassium chlorate when heated just above its melting point decomposes into potassium perchlorate and potassium chloride. This reaction is called disproportionation or auto-oxidation and auto-reduction. On heating further, $KClO_4$ decomposes to KCl and oxygen.

(iv) $4KClO_3 \longrightarrow 3KClO_4 + KCl$

$KClO_4 \longrightarrow KCl + 2O_2$

4. ACTION OF HEAT ON NITRATES

Generally heavy metal nitrates decompose to metal oxide, reddish brown nitrogen dioxide gas and oxygen.

(i) Lead nitrate decomposes to PbO, NO_2 & O_2.

$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 \uparrow$ & O_2.

litharge or lead (II) oxide (red when hot and yellos when cold)

(ii) Cupric ntrate decomposes to CuO, NO_2 & O_2.

$2Cu(NO_3)_2 \longrightarrow 2CuO + 4NO_2 + O_2$

(green) (black)

(iii) Zinc nitrate decomposes to ZnO, NO_2 & O_2. (zinc oxide, yellow when hot and white when cold)

Knowing the colours of some oxides will be useful in qualitative analysis.

(iv) Nitrates of mercury and silver, whose oxides are unstable, decompose into the metal, NO_2 and O_2.

$Hg(NO_3)_2 \longrightarrow Hg + 2NO_2 + O_2$

$2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2$

(v) Alkali metal nitrates decompose to give the metal nitrite and O_2 (No reddish brown NO_2 gas).

$2KNO_3 \longrightarrow 2KNO_2 + O_2$

$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$

(vi) Ammonium nitrate on heating leaves no residue and forms nitrous oxides and steam.

$NH_4NO_3 \longrightarrow N_2O + 2H_2O$

5. ACTION OF HEAT ON AMMONIUM COMPOUNDS

Generally an ammonium compound decomposes into ammonia and an acid or acidic oxide if the acid is unstable to heat.

(i) $NH_4Cl \longrightarrow NH_3 + HCl$

(ii) $(NH_4)_2SO_4 \longrightarrow 2NH_3 + H_2SO_4$

(iii) $(NH_4)_3PO_4 \longrightarrow 3NH_3 + H_3PO_4$

(iv) $(NH_4)_2CO_3 \longrightarrow 2NH_3 + CO_2 + H_2O$

(v) Ammonium compounds which do not ammonia on heating are ammonium nitrate, ammonium nitrite and ammonium dichromate.

$NH_4NO_3 \longrightarrow N_2O + 2H_2O$

$NH_4NO_2 \longrightarrow N_2 + 2H_2O$

$(NH_4)_2Cr_2O_7 \longrightarrow N_2 + 4H_2O + Cr_2O_3$

(Green fluffy chromic oxide)

6. ACTION OF HEAT ON METALLIC CARBONATES

(i) Generally metallic carbonates decompose to give metal oxide and CO_2.

$CaCO_3 \xrightarrow{900^\circ C} CaO + CO_2 \uparrow$

$MgCO_3 \longrightarrow MgO + CO_2 \uparrow$

$CuCO_3 \longrightarrow CuO + CO_2 \uparrow$

(pale green) (black)

$PbCO_3 \longrightarrow$ $PbO+CO_2\uparrow$

(yellow)

$ZnCO_3 \longrightarrow ZnO+CO_2\uparrow$

(ii) Carbonates of strongly electropositive meals (alkali metals except lithium) do not decompose on heating

(iii) Silver carbonate decomposes to give the metal, CO_2 & O_2.

$2Ag_2CO_3 \longrightarrow 4\,Ag+ 2CO_2+O_2$

(iv) Ammonium carbonate (smelling salt) decomposes to give NH_3, H_2O & CO_2. All the products are in gaseous phase and there is no residue left.

$(NH_4)_2CO_3 \longrightarrow 2NH_3+H_2O+CO_2$

7. ACTION OF HEAT ON METALLIC BICARBONATES

Only $NaHCO_3$ and $KHCO_3$ are solids; others are known in solution. All bicarbonates decomposes to give the metal carbonate, H_2O & CO_2.

$2NaHCO_3 \longrightarrow Na_2CO_3+H_2O+CO_2\uparrow$

$Ca(HCO_3)_2 \longrightarrow CaCo_3+H_2O+CO_2\uparrow$

$Mg(HCO_3)_2 \longrightarrow MgCO_3+H_2O+CO_2\uparrow$

8. ACTION OF HEAT ON CERTAIN HYDRATED CHLORIDES

Hydrated halides on heating are converted to oxides, H_2O and halo acids.

(i) $MgCl_2\ 6H_2O$ does not get completely dehydrated because $MgCl_2$ is hydrolysed by water to give basic $MgCl_2$.

$MgCl_2.6H_2O \longrightarrow Mg(OH)Cl+5H_2O+HCl$

(ii) $Al_2Cl_6\ .\ 12H_2O \longrightarrow Al_2O_3+\ 6HCl+9H_2O$

(iii) $SnCl_2.2H_2O$ undergoes hydrolysis to form basic chloride.

$SnCl_2.2H_2O \longrightarrow Sn(OH)Cl+H_2O+HCl$

(iv) On heating certain halides of metal ions in higher oxidation state changes to halides of lowwer oxidation state.

$2FeCl_3 \longrightarrow 2FeCl_2+Cl_2$

$2CuCl_2 \longrightarrow Cu_2Cl_2+Cl_2$

9. ACTION OF HEAT ON SOME OTHER COMPOUNDS

(i) When sodium sulphite is heated, it undergoes disroportionation reaction.

$4Na_2SO_3 \longrightarrow 3Na_2SO_4+Na_2S$

(ii) Sodium thiosulphate $Na_2S_2O_3 5H_2O$ loses water of hydration and becomes anhyrous salt, which on further heating gives a mixture of sodium sulphate, sodium sulphide and sulphur.

$Na_2S_2O_3.5H_2O \longrightarrow Na_2S_2O_3+5H_2O$

$4Na_2S_2O_3 \longrightarrow 3Na_2SO_4+Na_2S+4S$

(iii) When hydrated copper sulphate (blue vitrio) is heated) CuO & SO_2 formed.

$CuSO_4.5H_2O \xrightarrow{100^\circ C} CuSO_4H_2O+4H_2O$

$CuSO_4.H_2O \xrightarrow{230^\circ C} CuSO_4+H_2O$

$2SO_3 \longrightarrow 2SO_2+O_2$

(iv) Gypsum $CaSO_4$, when heated to 120–130°C froms a hemihydrate called Plaster of paris.

$CaSO_4.2H_2O \longrightarrow CaSO_4.\ ½\ H_2O + 3/2\ H_2O$

If heated above 200°C, it forms anhydrous calcim sulphate which does not set with water

(v) Green vitriol, $FeSO_4.7H_2O$, when heated forms Fe_2O_3, SO_2, & H_2O

$2FeSO_4.\ 7H_2O \longrightarrow Fe_2O_3 + SO_2 + SO_3 + 14H_2O$

(vi) $MgSO_4.\ 7H_2O \xrightarrow{\Delta} MgSO_4 + 7H_2O$

(Epsom salt)

(vii) $Al_2(SO_4)3.\ 18H_2O \xrightarrow{\Delta} Al_2O_3 + 3SO_3 + 18H_2O$

(purple) (white)

(viii) $Cr_2(SO_4)_3.\ 18H_2O \xrightarrow{\Delta} Cr_2O_3 + 3SO_3 + 18H_2O$

(green)

(ix) $Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3$

(yellow) (blackish brown)

(x) $2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_3 + SO_2$

(light green)

10. ACID-BASE REACTIONS

(i) A strong acid liberates a relatively weaker acid from its salt. The common strong acids are perchloric acid, sulphuric acid, hydrocyanic acid and most of organic acids. Thus concentrated sulphuric acid displaces most acids from their salts.

$KCl + H_2SO_4 \longrightarrow KHSO_4 + HCl$

$KNO_3 + H_2SO_4 \longrightarrow KHSO_4 + HNO_3$

$Ca_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 3CaSO_4 + 2H_3PO_4$

$CH_3COONa + HCl \longrightarrow CH_3COOH + NaCl$

(ii) Almost all acids displace carbonic acid from carbonates and bicarbonates. Since carbonic acid is unstable, it decomposes liberating CO_2 with effervesence (Test for acids).

$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2\uparrow$

$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2\uparrow$

$KHCO_3 + HNO_3 \longrightarrow KNO_3 + H_2O + CO_2\uparrow$

(iii) A strong base can displace a weak base from a salt of strong acid and weak base.

$NH_4Cl + NaOH \longrightarrow NaCl + NH_4OH$

11. SOME OTHER USEFUL REACTIONS

(iv) $2BaCrO_4 + 6KI + 8H_2SO_4 \longrightarrow 3I_2 + 3BaSO_4 + 3K_2SO_4 + Cr_2(SO_4)_3 + 8H_2O$

(v) $2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + I_2 + 2K_2SO_4$

(vi) $3MnO_4^- + 5C_2O_4^{-2} + 16H^+ \longrightarrow 3Mn^{+2} + 10CO_2 + 8H_2O$

METHODS OF BALANCING CHEMICAL REACTIONS

A balanced chemical reaction must of follow the conservations of atoms of each elements mass and charge. Any chemical reaction can be balaced by conserving the atoms of each elements and charges. By the knowledge of oxidation and reduction, any redox reaction can be balanced by using either oxidation number method or by ion electron method.

(1) OXIDATION NUMBER METHOD:

The method is based on the fact the total change in oxidaton state in oxidation and reduction

should be equal for a balanced reaction. A redoc reaction be balanced by making the total changes in oxidation states in oxidation and reduction processes, equal A reaction can be balanced by oxidation number method by using the following steps:

Step I: Select the species undergoing oxidation and reduction and write both the processes, separately

Step II: Balance the atoms of responsible elements (elements responsible for change in oxidation state) by simple counting.

Step III: Determine the changes in oxidation state of both the process, due to the total number of atoms of responsible elements.

Step IV: Make the changes is oxidation state of both processes, equal by multiplying with suitable numbers. Add both the processes after multiplication.

Step V: If some reaction components are left, write them in proper side and balance them by simple counting.

Step IV: If the reaction is not balancing at step IV or V, add some molecule or ion in the proper side, The species added should be according to the reaction and it should not create a new change in oxidation state.

Example : Balance the following reactions by oxidation number method

(A) $KMnO_4+H_2SO_4+HCl \longrightarrow K_2SO_4 + MnSO_4 + H_2O + Cl_2$

Solution:

Step I: Oxidation: $\overset{-1}{H}\overset{}{Cl} \longrightarrow \overset{0}{Cl_2}$

Reduction: $K\overset{+7}{M}nO_4 \longrightarrow \overset{+2}{M}nSO_4$

Step II: Oxidation: $2HCl \longrightarrow Cl_2$

Reduction: $KMnO_4 \longrightarrow MnSO_4$

Change is O.S.

Step III: Oxidation: $2\overset{-1}{H}\overset{}{Cl} \longrightarrow \overset{0}{Cl_2}$ 2

Rediuction: $K\overset{+7}{M}nO_4 \longrightarrow \overset{+2}{M}nSO_4$ 5

Change is O.S.

Steep IV: Oxidation: $2HCl \longrightarrow Cl_2$ 2]×5

Reduction: $KMnO_4 \longrightarrow MnSO_4$ 5]×2

$2KMnO_4+10\,HCl \longrightarrow 2MnSO_4 + 5Cl_2$

Step V: $2KMnO_4+10HCl + 3H_2SO_4 \longrightarrow 2MnSO_4 + 5\,Cl_2+K_2SO_4+8H_2O$ is the balanced reaction.

(B) $\mathbf{Cl_2+NaOH \longrightarrow NaCl + NaClO_3 + H_2O}$

Solution:

Step I: Oxidation: $\overset{0}{Cl_2} \longrightarrow Na\overset{+5}{Cl}O_3$

Reduction: $\overset{0}{Cl_2} \longrightarrow Na\overset{-1}{Cl}$

Step II: Oxidation: $Cl_2 \longrightarrow 2NaClO_3$

Reduction: $Cl_2 \longrightarrow 2NaCl$

Change is O.S.

Step III: Oxidation: $2\overset{0}{Cl}_2 \longrightarrow \overset{+1}{NaCl}$ 10

Rediuction: $\overset{0}{Cl}_2 \longrightarrow 2\overset{-1}{NaCl}$ 2

Change is O.S.

Steep IV: Oxidation: $Cl_2 \longrightarrow 2NaClO_3$ 10

Reduction: $KMnO_4 \longrightarrow 2NaCl$ 2]×5

$6Cl_2 \longrightarrow 2NaClO_3 + 10NaCl$

or, $3Cl_2 \longrightarrow NaClO_3 + 5NaCl$

Step V: $3Cl_2 + 6NaOH \longrightarrow NaClO_3 + 5NaCl + 3H_2O$ is the balanced reaction.

(C) $\mathbf{Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + NO + H_2O}$

Solution:

Step I: Oxidation: $\overset{0}{Zn} \longrightarrow \overset{+2}{Zn}(NO_3)_2$

Reduction: $\overset{+5}{HNO_2} \longrightarrow \overset{+2}{NO}$

Step II: Oxidation: $\overset{0}{Zn} \longrightarrow \overset{+2}{Zn}(NO_3)_2$

Reduction: $\overset{+5}{HNO_3} \longrightarrow \overset{+2}{NO}$

Change is O.S.

Step III: Oxidation: $\overset{0}{Zn} \longrightarrow \overset{+2}{Zn}(NO_3)_2$ 2

Rediuction: $\overset{+5}{HNO_3} \longrightarrow \overset{+2}{NO}$ 3

Change is O.S.

Steep IV: Oxidation: $Zn \longrightarrow Zn(NO_3)_2 + 2NO$ 2]×3

Reduction: $HNO_3 \longrightarrow 3Zn(NO_3)_2 + 2NO + H_2O$ 3]×2

$3Zn \longrightarrow 3Zn(NO_3)_2 + 2NO$

Step V: $3Zn + 2HNO_3 \longrightarrow 3Zn(NO_3)_2 + 2NO + H_2O$

The reaction cannot be balanced without changing the stoichiometric coefficient of HNO_3.

Step IV: Add six molecules of HNO_3 in the left side in order to balance the number of nitrogen atoms

$3Zn + 2HNO_3 + 6HNO_3 \longrightarrow 3Zn(NO_3)_2 + 2NO + H_2O$

or, $3Zn + 8HNO_3 \longrightarrow 3Zn(NO_3)_2 + 2NO + 4H_2O$ is the balanced reaction.

(2) ION ELECTRON METHOD:

The method is based on the fact that the total loss of electron in oxidaton and total gain of electron in reduction, should be equal for a balanced reaction. A redox reaction may be balanced by making the total number of electrons lost and gained in oxidaton and reduction processes, equal. A reaction may be balanced by ion electron method by using the following steps:

Step I: If the reaction is given in molecular form, convert it in the ionic form. For it, write strong acids, strong bases and all water soluble salts in ionic form and then cancel out the spectator ions (ions common in both sides).

Step II: Select the species undergoing oxidation and reduction and write them separately.

Step III: Balance the atoms of responsible element by simple counting.

Step IV: Balance the atoms of all other elements by adding some molecule or ion in the proper side. The species added should be according to the reaction and it should not create not create any new change in the oxidation state. In most of the reaction, the other elements are hydrogen or oxygen. They are balanced according to medium of the reaction.

In acidic medium:

→ Add one water molecule in the opposite side for each excess of oxygen atom.

→ Add one H^+ ion in the opposite side for each excess of hydrogen atom.

In basic medium:

→ Add one water molecule in the same side and two OH^- ions in opposite side for each excess of oxygen atom.

→ Add one OH^- ion in the same side and one water molecule in the opposite side for each excess of hydrogen atom.

→ Hydrogen and oxygen atoms may also be balanced by balanced by balancing them first in acid medim and then replacing the H^+ ions suitably by OH^- ions. For it, add OH^- ions equal in number to the H^+ ions in both the sides and then write the combination of one OH^- ion and one H^+ ion ions as an H_2O molecule. It must be noted that the combination of one H^+ and one OH^- ions, in ionic form of a reaction.

Step V: Balance the charges in both process by addding proper number of electron in the proper side. The number of electrons added and the side, in which they are added, can be checked.

→ In oxidation, electrons will be added in the right side and in the reduction, left side.

→ The number of electrons lost or gained will always be equal to the change in oxidation state.

→ The number of elecrons lost or gained in a particular process in independent to the medium of reaction.

Step VI: Make the total number of electrons lost and gained equal by multiplying with suitable numbers. Add both the processes. It should be balanced reaction in ionic form.

Step VII: If the original reaction was in molecular form, convert the ionic form into molecular form.

Example 4: Balance the following reactions by ion elecron method:

(A) $KMnO_4+H_2SO_4+HCl \longrightarrow K_2SO_4+MnSO_4+Cl_2+H_2O$

Solution:

Step I: Ionic form of the given reaction is

$K^+ + MnO_4^- + 2H^+ + SO_4^{2-} + H^+ + Cl^- \longrightarrow 2K^+ + SO_4^{2-} + Mn^{2+} + SO_4^{2-} + Cl_2 + H_2O$

or $MnO_4^- + H^+ + Cl^- \longrightarrow Mn^{2+} + Cl_2 + H_2O$

Step II: Oxidation: $Cl^- \longrightarrow \overset{0}{Cl_2}$

Reduction: $\overset{+7}{MnO_4}^- \longrightarrow Mn^{2+}$

Step III: Oxidation: $2Cl^- \longrightarrow Cl_2$

Reduction: $MnO_4^- \longrightarrow Mn^{2+}$

Step IV: Oxidation: $2Cl^- \longrightarrow Cl_2$

Reduction: $MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$

Step V: Oxidation: $2Cl^- \longrightarrow Cl_2 + 2e$

Reduction: $MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$

Step VI: Oxidation: $2Cl^- \longrightarrow Cl_2 + 2e$] × 5

Reduction: $MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$] × 2

$2MnO_4^- + 16H^+ + 16H^+ + 10Cl^- \longrightarrow 2Mn^{2+} + 8H_2O + 5Cl_2$

It is balanced reaction in ionic form.

Step VII: $2KMnO_4 + 10\ HCl + 3H_2SO_4 \longrightarrow 2MnSO_4 + 8\ H_2O + 5Cl_2 + K_2SO_4$ is the balanced reaction.

(B) $\mathbf{Cl_2 + OH^- \longrightarrow ClO_3^- + Cl^- + H_2O}$

Step I: Oxidation: $Cl_2 \longrightarrow ClO_3^-$

Reduction: $Cl_2 \longrightarrow Cl^-$

Step II: Oxidation: $Cl_2 \longrightarrow 2ClO_3^-$

Reduction: $Cl_2 \longrightarrow 2Cl^-$

Step III: Oxidation: $Cl_2 + 12OH^- \longrightarrow 2ClO_3^- + 6H_2O$

Reduction: $Cl_2 \longrightarrow 2Cl^-$

Step IV: Oxidation: $Cl_2 + 12OH^- \longrightarrow 2ClO_3^- + 6H_2O + 10e$

Reduction: $Cl_2 + 2e \longrightarrow 2Cl^-$

Step V: Oxidation: $Cl_2 + 12OH^- \longrightarrow 2ClO_3^- + 6H_2O + 10e$

Reduction: $Cl_2 + 2e \longrightarrow 2Cl^-$] ×5

$6Cl_2 + 12OH^- \longrightarrow 2ClO_3^- + 10Cl^- + 6H_2O$

or $3Cl_2 + 6\ OH^- \longrightarrow ClO_3^- + 5Cl^- + 3H_2O$ is the balanced reaction.

Step III onwards may be replaced as:

Step III: Oxidation: $Cl_2 + 6H_2O \longrightarrow 2ClO_3^- + 12H^+$

Reduction: $Cl_2 \longrightarrow 2Cl^-$

Step IV: Oxidation: $Cl_2 + 6H_2O \longrightarrow 2ClO_3^- + 12H^+ + 10e$

Reduction: $Cl_2 + 2e \longrightarrow 2Cl^-$

Step V: Oxidation: $Cl_2 + 6H_2O \longrightarrow 2ClO_3^- + 12H^+ + 10e$

Reduction: $Cl_2 + 2e \longrightarrow 2eCl^-$] ×5

$6Cl_2 + 12OH^- \longrightarrow 2eCl^- + 10Cl^- + 6H_2O$

or, $3Cl_2 + 3H_2O \longrightarrow ClO_3^- + 5Cl^- + 6H^+$

To remove H^+ ion, add equal number of OH^- ions in both sides.

$3Cl_2 + 3H_2O + 6OH^- \longrightarrow ClO_3^- + 5Cl^- + 6H^+ + 6OH^-$

or, $3Cl_2 + 3H_2O + 6OH^- \longrightarrow ClO_3^- + 5Cl^- + 6H_2O$

or, $3Cl_2 + 6OH^- \longrightarrow ClO_3^- + 5Cl^- + 3H_2O$ is the balanced reaction.

EQUIVALENT CONCEPT

EQUIVALENT WEIGHT

Equivalent weight of any substance may be defined as the grams of the substance corresponding to the loss or gain of one mole of electron. In case of acid-base reactions, the equivalent weight of any substance is the number of grams of the substance involed in the loss or gain of one mole of proton. For simplicity, we formulate the equivalent weight of differently.

EQUIVALENT WEIGHT OF AN ELEMENT

It is the number of gm of the element which combines with or displaces 1 gm hydrogen or 8 gm of oxygen or 35.5gm of chlorine.

It the atomic weight of an element is A and its valency is V, then its equivalent weight is, $E=\frac{A}{V}$

Example Determine the equivalent weight of underlined element in the following compounds:

(i) $\underline{P}H_3$ (ii) $\underline{S}O$

Sol. (i) $E_p = \frac{\text{Atomic weight}}{\text{Valency}} = \frac{31}{3} =$ **10.33**

(ii) $E_S = \frac{\text{Atomic weight}}{\text{Valency}} = \frac{32}{6} =$ **5.33**

Example : An oxide of a metal contains 40% oxygen, by weight. What is the equivalent weight of the metal ?

Sol: Let we have 100 gm of metal oxide. From question, it will contain 40 gm oxygen and (100–40)=60 gm metal, Now,

$\therefore$ 40 gm oxygen is combined with 60 gm metal

$\therefore$ 8 gm oxygen will combine with $\frac{60}{40}\times 8 = 12$ gm metal

Hence, equivalent weight of metal = **12**.

PRINCIPLE OF G-EQUIVALENCE

Number of g-equivalents of all the reactants will be equal and the same number of g-equivalents of each product will form. It is due to the fact that equivalent weight of any substance is its weight corresponding to the loss or gain of one mole of electron or proton (in non-redox reactions). As the equivalent weights of all substances present in a reaction are determined on the same reference, their number of g-equivalents must be same.

Ex.: 5.04 gm of metal carbonate produces 2.4 gm metal oxide on complete decomposition. What is the equivalent weight of metal ?

Sol. No. of g-eq. of metal carbonate = no. of g-eq. of metal oxide.

or, $\left(\frac{W}{E}\right)_{\text{metal carbonate}} = \left(\frac{W}{E}\right)_{\text{metal oxide}}$

or, $\frac{5.04}{E+30} = \frac{2.4}{E+8}$

$\therefore$ Equivalent weight of metal, E=**12**

(A) Volumetric analysis :

This mainly involve titrations based chemistry. If can be divided into two major category.

(I) Non-redox system (II) Redox system

(I) Non-redox system

This involve following kind of titrations :

1. Acid-Base titrations
2. Back titration
3. Precipitation titration
4. Double indicator acid base titration

Titrimetric Method of Analysis :

A titrimetric method of analysis is based on chemical reaction such as.

$$aA + tT \rightarrow \text{Product.}$$

Where 'a' molecules of "analysis", A reacts with t molecules of reagent T.

T is called Titrant normally taken in buret in form of solution of known concentration. The solution of titrant is called "standard solution".

The addition of titrant is added till the amount of T, chemically equivalent to that of 'A' has been added. It is said equivalent point of titration has been reached. In order to know when to stop addition of titrant, a chemical substance is used called indicator, which respond to appearance of excess of titrant by changing colour precisely at the equivalence point. The point in the titration where the indicator changes colour is termed the 'end point'. It is possible that end point be as close as possible to the equivalence point. The term titration refer's to process of measuring the volume of titrant required to reach the end point.

Law of Chemical equivalence :

It states that in any chemical reaction the equivalents of all the reactants and products must be same.

$2A + 3B \rightarrow 4C$

Eg. of A = Equivalents of 'B' = Equivalents of 'C'

$$\text{Equivalents of 'A'} = \frac{\text{Weight of 'A'}}{\text{Equivalent weight of 'A'}}$$

or Equivalents of 'A' = no. of moles of 'A' × n-factor

$A + B + C \rightarrow$ product

If A & B do not react with each other but C react with both A & B then

gm eq. of A + gm eq. of B = gm eq. of C

or

meq. of A + meq. of B = meq. of C

n - factor calculation

n factor here we mean a conversion factor by which we divide molar mass of substance to get equivalent mass and it depends on nature of substance which vary from one condition to another condition. We can divide n-factor calculations in two category.

(1) In case of non-redox reaction.

(a) n factor of acid = basicity of the acid

Basicity : Number of replacible H^+ ion.

Ex. n factor of HCl = 1

n factor of CH_3COOH = 1

n factor of H_2SO_4 = 2

(b) n factor of base = acidity of the base

Acidity : Number of replaceble OH^- ion.

Ex. n factor of NaOH = 1

n factor of $Ca(OH)_2$ = 2

n factor of $Al(OH)_3$ = 3

n factor of $B(OH)_3$ = 1 (because it is a mono basic acid)

(c) n factor Salt : Total number of positive or negative charge.

Ex. n factor of NaCl = 1

n factor of Na_2SO_4 = 2

n factor of $K_2SO_4.Al_2(SO_4)_3.24H_2O$ = 8

Ex. Find the n factor of H_3PO_4 in the following reaction.

$$H_3PO_4 + Ca(OH)_2 \rightarrow CaHPO_4 + 2H_2O$$

Sol. Basicity of H_3PO_4 in the above reaction is 2

$\therefore$ the n factor of H_3PO_4 is 2

(2) In case of redox reaction.

(a) From oxidation number

n factor of oxidising or redusing agent = change in oxidation number per molecule.

$\Rightarrow$ consider a salt A_xB_y in which the O.S. of A is +c. It changes to a compound A_dE in which the O.S. of A is +f. Here we are assuming that B does not undergo any change in O.S.

$A_x^{+c} B_y \rightarrow A_d^{+f} E$ (obviously A_xB_y must have reacted with some other substance to produce the product A_dE. That means other substance has the atom E in it.)

The 'n' factor is = |xc – xf |.

Ex. Find the n factor of $KMnO_4$ in different medium.

Sol. (i) In acidic mediam

$KMnO_4 \rightarrow Mn^{+2}$

Change in oxidation number of Mn = +7 – 2 = 5

$\therefore$ the n factor of $KMnO_4$ = 5 **Ans.**

(ii) strongly basic medium

$KMnO_4 \rightarrow K_2MnO_4$

n factor of $KMnO_4$ = +7 – 6 = 1 **Ans.**

(iii) neutral medium or weakly basic medium

$KMnO_4 \rightarrow MnO_2$

n factor of $KMnO_4$ = +7 – 4 = 3 **Ans.**

Ex. Find the n factor of $Na_2S_2O_3$ in the following reactions.

(a) $Na_2S_2O_3 + I_2 \rightarrow NaI + Na_2S_4O_6$

(b) $Na_2S_2O_3 + I_2 \rightarrow NaI + Na_2SO_4$

Sol. (a) Change in oxidation number of sulphur = |+2 – 2.5| = 0.5

Change in oxidation number per molecule = 0.5 × 2

$\therefore$ n factor of $Na_2S_2O_3$ = 1

(b) Change in oxidation number of sulphur = |2 – 6| = 4

Change in oxidation number per molecule = 4 × 2

$\therefore$ n factor of $Na_2S_2O_3$ = 8

$\Rightarrow$ Consider the salt A_xB_y to undergo a reaction so that the element A undergoes a change in O.S. but is present in more than one product with the same O.S. i.e.

$A_x^{+c}By \rightarrow A_a^{+f} + A_{x-a}^{+f} + yB^{-\frac{xc}{y}}$ (the superscripts denote the oxidation state of the respective elements).

$\therefore$ n = |xc – xf|

$\Rightarrow$ Salts that react in such a way that more than one type of atom in the salt undergoes O.S. change.

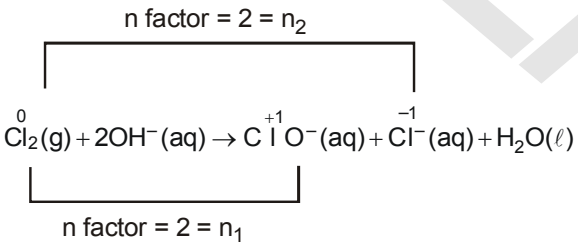
$E + A_x^{+c}By \rightarrow A_a^{+f}E + J_xB^{-1}$

In this case both A and B are changing their O.S.'s and both of them are either getting oxidised or reduced. In such a case n factor of the compound is the sum of the individual n factors of A and B. i.e. |xc – xf| + | –xC – (–yi)|. Then n factor of A can be undersood which is |xc – xf|. The n factor of B is |–xc – (–yi)|

Disproportionation Reactions :

A redox reaction in which a same element present in a particular compound in a definite oxidation state is oxidized as well as reduced simultaneously is a disporportionation reactions.

Ex.



n factor of overall reaction = $n_1 \times n_2 / n_1 + n_2$

(b) From ion electron method :

n factor = total number of electrons transfered per mole of the reactant

Ex. $MnO_4^- + 8H^+ + 5e \rightarrow Mn^{+2} + 4\,H_2O$

n factor of $KMnO_4$ = 5

Acid-Base titration.

To find out strength or concentration of unknown acid or base it is titrated against base or acid of known strength. At the equivalence point we can know amount of acid or base used and then with the help of law of equivalents we can find strength of unknown.

Meq of acid at equivalence point = Meq of base at equivalence point

Ex. **One litre solution of alkali (NaOH) is prepared by dissolving impure solid of alkali which contain 5% Na_2CO_3 and 8% $CaCO_3$ and 10% NaCl. A 10 ml portion of this solution required 9.8 mL of a 0.5 M H_2SO_4 solution for neutralization. Calculate weight of alkali dissolved initially.**

gm eq. of Na_2CO_3 + gm eq. of $CaCO_3$ + gm eq. of NaOH = gm eq. of H_2SO_4

Sol. $\frac{5x}{100}\times\frac{1}{53}+\frac{8x}{100}\times\frac{1}{50}+\frac{77x}{100}\times\frac{1}{40}=0.98$ x = 45 g **Ans.**

Back titration

Back titration is used in volumetric analysis to find out excess of reagent added by titrating it with suitable reagent. it is also used to find out percentage purity of sample. For example in acid-base titration suppose we have added excess base in acid mixture. To find excess base we can titrate the solution with another acid of known strength.

Ex. **20 g. of a sample of $Ba(OH)_2$ is dissolved in 50 ml. Of 0.1 N HCl solution. The excess of HCl was titrated with 0.1 N NaOH. The volume of NaOH used was 20 cc. Calculate the percentage of $Ba(OH)_2$ in the sample.**

Sol. Milli eq. of HCl initially = 50 × 0.1 = 5

Milli eq. of NaOH consumed = Milli eq. of HCl in excess = 20 × 0.1 = 2

$\therefore$ Milli eq. of HCl consumed = Milli eq. of $Ba(OH)_2$ = 5 – 2 = 3

$\therefore$ eq. of $Ba(OH)_2$ = 3/1000 = 3×10^{-3}

Mass of $Ba(OH)_2$ = $3\times10^{-3}\times(171/2)$ = 0.2565 g.

% $Ba(OH)_2$ = (0.2565/20) × 100 = 1.28 % **Ans.**

Precipitation titration :

In ionic reaction we can know strength of unknown solution of salt by titrating it against a reagent with which it can form precipitate. For example NaCl strength can be known by titrating it against $AgNO_3$ solution with which it form white ppt. of AgCl.

So meq. of NaCl at equivalence point = meq. of $AgNO_3$ used = meq. of AgCl formed

Ex. **A complex of cobalt with ammonia is analyzed for determining its formula, by titrating it against a standardized acid as follows :**

$Co(NH_3)_x Cl_3(aq) + HCl \rightarrow NH_4^+(aq) + Co^{3+}(aq) + Cl^-(aq)$

A 1.58 g complex required 23.63 mL 1.5 M HCl to reach the equivalence point. Determine formula. If the reaction mixture at equivalence point is trated with excess of $AgNO_3$ solution, what mass of AgCl will precipitate out ?

Sol. The balanced chemical reaction is :

$Co(NH_3)_xCl_3 + xHCl \rightarrow xNH_4^+ + Co^{3+} + (x+3)\,Cl^-$

$\frac{1.58}{165.5+17x}$ $\frac{1.58x}{165.5+17x}$ $\frac{1.58(x+3)}{165.5+17x}$

$\Rightarrow \frac{1.58x}{165.5+17x}=\frac{23.63\times1.5}{1000}$ = moles of HCl, x = 6

moles of Cl = moles of AgCl = $\frac{(x+3)\times 1.58}{165.5+17x}$, wt. of AgCl = $\frac{(x+3)\times 1.58}{165.5+17x}\times 143.5 = 7.62$

m(AgCl) = 0.053 × 143.5 = 7.62 g **Ans.**

Double indicator acid-base titration :

In the acid-base titration the equivalence point is known with the help of indicator which changes its colour at the end point. In the titration of polyacidic base or polybasic acid there are more than one end point. One indicator is not able to give colour change at every end point. So to find out each end point we have to use more than one indicator. For example in the titration of Na_2CO_3 against HCl there are two end points.

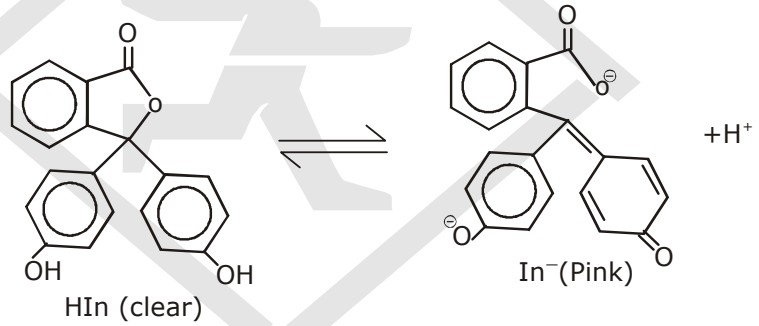
$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$

$NaHCO_3 + HCl \rightarrow H_2CO_3 + NaCl$

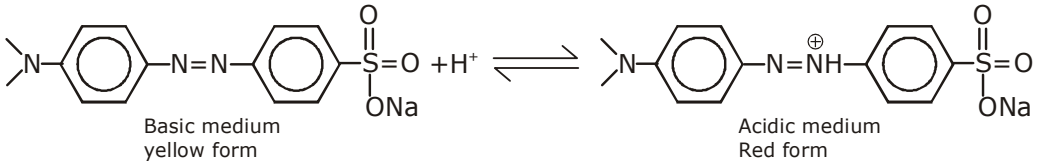
When we use phenolphthalein in the above titration it changes its colour at first end point when $NaHCO_3$ is formed and with it we can not know second end point. Similarly with methyl orange it changes its colour at second end point only and we can not know first end point. it is because all indicator changes colour on the basis of pH of medium. So in titration of $NaHCO_3$, $KHCO_3$ against acid phenolphthalein can not be used.

Titration	Indicator	pH Range	n factor
Na_2CO_3 ┐ against acid	Phenolphthalein	8.3 – 10	1
Na_2CO_3 ┘ against acid	Methyl orange	3.1 – 4.4	2

Phenophthalein



Methyl orange



A sample contains NaOH, Na_2CO_3 & $NaHCO_3$. This solution is titrated with HCl or H_2SO_4

(i) When Phenolphthalein (HPh) is used as indicator the reaction are given below.

$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$

This is the Half neutralisation of Na_2CO_3

$NaHCO_3 + HCl \rightarrow X$

$NaOH + HCl \rightarrow NaCl + H_2O$

Hence

$$\text{Meq. of HCl} = \text{meq of NaOH} + \frac{1}{2}\text{ meq. of } Na_2CO_3$$

(ii) when methyl orange (MeOH) is used as indicator

$Na_2CO_3 + 2HCl \rightarrow 2\,NaCl + H_2O + CO_2$

This is the complete neutralisation

$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$

$NaOH + HCl \rightarrow NaCl + H_2O$

in this case

meq. of HCl = meq of NaOH + meq. of Na_2CO_3 + meq. of $NaHCO_3$

(iii) If MeOH is added after the first end point obtained from HPh

$NaHCO_3$ + $NaHCO_3$ + $HCl \rightarrow NaCl + H_2O + CO_2$

Produced original

meq. of HCl = meq. of $NaHCO_3$ (produced) + meq. of $NaHCO_3$ (original)

Note : When we carry out dilution of solution, meq eq. milli mole or mole of substance does not change because they represent amount of substance, however molar concentration may change.

Ex. **A solution contains a mixture of Na_2CO_3 and NaOH. Using phenolphthalein as indicator 25 ml. of mixture required 19.5 ml of 0.995 N HCl for the end point. With methyl orange. 25 ml of solution required 25 ml. of the same. HCl for the end point. Calculate grams per litre of each substance in the mixture.**

Sol. meq of $Na_2CO_3 = 2 \times$ moles $Na_2CO_3 = a$

meq of NaOH = $b = 1 \times$ moles of NaOH

with phenol phthalein

$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$ nf=1

$NaOH + HCl \rightarrow NaCl + H_2O$ nf=1

$\therefore$ a/2+b=meq of HCl=19.5×0.995=19.4

with methyl orange

$Na_2CO_3 + HCl \rightarrow NaCl + H_2CO_3$ nf=2

$NaOH + HCl \rightarrow NaCl + H_2O$ nf=1

a+b=meq of HCl = 25×.995=24.875

$a/2 = 5.475 \Rightarrow a = 10.95,\ b = 13.925$

$$\text{wt of } Na_2CO_3\text{/lit} = \frac{10.95}{25} \times 10^{-3} \times \frac{106}{2} \times 1000 = 23.2 \text{ gm/lit}$$

wt of NaOH/lit = $b \times 10^{-3} \times 84/25 \times 1000 = 22.28$ gm/lit

CALCULATION OF AVAILABLE CHLORINE FROM A SAMPLE OF BLEACHING POWDER

The weight % of available Cl_2 from the given sample of balaching powder on reaction with dil acids or CO_2 is called available chlorine.

$CaOCl_2 + H_2SO_4 \rightarrow CaSO_4 + H_2O + Cl_2$

$CaOCl_2 + 2HCl \rightarrow CaCl_2 + H_2O + Cl_2$

$CaOCl_2 + 2CH_3COOH \rightarrow Ca(CH_3COO)_2 + H_2O + Cl_2$

$CaOCl_2 + CO_2 \rightarrow CaCO_3 + Cl_2$

Method of determination :

Bleaching powder + CH_3COOH + KI $\xrightarrow[\text{Hypo}]{\text{starch}}$ end point

meq. of I_2 = meq. of Cl_2 = meq. of Hypo solution

$$\% \text{ of } Cl_2 = \frac{3.55 \times x \times V(mL)}{W(g)}$$

where x = molarity of hypo solution

v = mL. of hypo solution used in titration.

Ex. 10 gm sample of bleaching powder was dissolved into water to make the solution on litre. To this solution 35 mL of 1.0 M Mohr salt solution was added containing enough H_2SO_4. After the reaction was complete, the excess Mohr salt required 30 mL of 0.1 M $KMnO_4$ for oxidation. The % of available Cl_2 approximately is (mol wt = 71)

Sol. meq. of Mohr's salt = 35 × 1 × 1 = 35

meq. of $KMnO_4$ = meq. of excess mohr salt = 30 × 0.1 × 5 = 15

meq. of Mohr salt reacted with bleaching powder = 35 – 15 = 20

meq. of Cl_2 = 20

wt. of $Cl_2 = 20 \times 10^{-3} \times \frac{71}{2} = 0.71$ gm

$\% \text{ of } Cl_2 = \frac{0.71}{2} \times 100 = 7.1\ \%$ **Ans.**

Expression of harness: Hardness is expressed in ppm of $CaCO_3$ equivalent to all hardness creating salts

$$\text{Hardness of water} = \frac{\text{g of } CaCO_3}{10^6 \text{ g of water}}$$

Example : 100 mL of a sample of tap water requires 50 mL of N/50 -HCl solution for titration. Calculate the temporary hardness of tap water.

Solution: HCl is required to react with bicarbonates present in water. Hence,

n_{eq} HCl= n_{eq} metal bicarbonatcs = n_{eq} $CaCO_3$

$$\text{or, } \frac{50 \times \frac{1}{50}}{1000} = \frac{W}{50}$$

or, w=0.05 gm

Hence, temporary hardness = $\frac{0.05}{100} \times 10^6$ = 500 ppm of $CaCO_3$

MODIFICATIONS IN LAW OF EQUIVALENCE

There are certain modifications required in order to use law of equivalence. These modifications are

(i) The equivalents of a substance produced and reacted mya not necessarily be same. If the n-factor of the substance, in the reaction in which it is produced were different than the n-factor of the same

substance, when it is reacting, then the equivalent of the substance produced and reacted would be different.

(ii) The equivalents of the same substances can be added or substracted only when they are of the similar n-factor.

(iii) In a reaction, the equivalents of oxidising agents would always be equal to the equivalents of reducing agents, irrespective of the number of agents usd in the reaction.

HARDNESS OF WATER

Water hardness is the traditional measure of the capacity of water to react with soap, hard water aquiring considerably more soap to produce a lather. Hard water often produces a noticeable deposit of precipitate (e.g. insoluble metals, soaps or salts) in containers, including "bathtub ring". It is not caused by a single substance but by a variety of dissolved polyvalent metallic ions, predominantly calcium and magnesium cations, although other cations (e.g. aluminium, barium, iron, manganese, strontium and zinc) also contribute. Hardness is most commonly expressed as milligrams of calcium carbonate equivalent per litre. Water containing calcium carbonate at concentrations below 60 mg/l is generally considered as soft; 60–120 mg/l, moderately hard; 120–180 mg/l, hard; and more than 180 mg/l, very hard (McGowan, 2000). Although hardness is caused by cations, it may also be discussed in terms of carbonate (temporary) and non-carbonate (permanent) hardness.

Temporary hardness

Temporary hardness is a type of water hardness caused by the presence of dissolved bicarbonate minerals (calcium bicarbonate and magnesium bicarbonate). When dissolved these minerals yield calcium and magnesium cations (Ca^{2+}, Mg^{2+}) and carbonate and bicarbonate anions (CO_3^{2-}, HCO_3^-). The presence of the metal cations makes the water hard. However, unlike the permanent hardness caused by sulfate and chloride compounds, this "temporary" hardness can be reduced either by boiling the water, or by the addition of lime (calcium hydroxide) through the softening process of lime softening. Boiling promotes the formation of carbonate from the bicarbonate and precipitates calcium carbonate out of solution, leaving water that is softer upon cooling.

Permanent hardness

Permanent hardness is hardness (mineral content) that cannot be removed by boiling. When this is the case, it is usually caused by the presence of calcium and magnesium sulfates and/or chlorides in the water, which become more insoluble as the temperature increases. Despite the name, the hardness of the water can be easily removed using a water softener, or ion exchange column.

SOFTENING OF WATER.

The process of the removal of hardness from water is called softening of water.

(a) Removal of temporary hardness: It can be removed by the following methods,

1. By boiling : During boiling, the bicarbonates of Ca and Mg decompose into insoluble carbonates and give CO_2. The insoluble carbonates can be removed by filtration.

$$Ca(HCO_3)_2 \xrightarrow{\text{Heat}} CaCO_3\downarrow + CO_2 + H_2O$$

$$Mg(HCO_3)_2 \xrightarrow{\text{Heat}} MgCO_3\downarrow + CO_2 + H_2O$$

2. Clark's method : Thisprocess is used on a commercial scale. Inthis process, calculated amount of lime [$Ca(OH)_2$] is added to temporary hard water.

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow MgCO_3\downarrow + CaCO_3\downarrow + 2H_2O$$

Soluble Lime (Insoluble)

(b) Removal of permanent hardness: Permanent hardness can be removed by the following methods,

1. By washing soda method: In this method, water is treated with a calculated amount of washing soda (Na_2CO_3) which converts the chlorides and sulphates of Ca and Mg into their respective carbonates which get precipitated.

$$CaCl_2 + Na_2CO_3 \downarrow + CaCO_3 + 2NaCl \rightarrow MgSO_4 + Na_2CO_3 \downarrow MgCO_3 + Na_2SO_4$$

2. Permutit method: This is a modern method employed for the softening of hard water. hydrated sodium aluminium silicate ($Na_2Al_2Si_2O_8.xH_2O$) is called permutit. These complex salts are also known as zeolites.

The permutit as loosely packed in a big tank over a layer of coarse sand. Hard water is introduced into the tank from the top. Water reaches the bottom of the tank and then slowly rises through the permutit layer in the tank. The cations present in hard water are exchanged for sodium ions. Therefore this method is also called ion exchange method.

$$\underset{\text{Sodium zeolite}}{Na_2Z} + \underset{\text{(From hard water)}}{Ca^{+2}} \longrightarrow \underset{\text{Cal. Zeolite}}{CaZ} + 2Na^+$$

$$\underset{\text{Sodium zeolite}}{Na_2Z} + \underset{\text{(From hard water)}}{Mg^{+2}} \longrightarrow \underset{\text{Mag. Zeolite}}{MgZ} + 2Na^+$$

where $Z = Al_2Si_2O_8.xH_2O$

3. Removal of permanent hardness by ion exchange

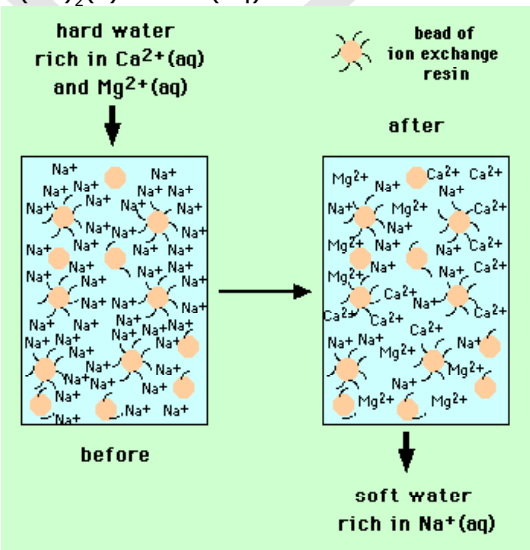
Ion exchange involves the swapping of calcium and magnesium ions for sodium ions.

$resin\text{-}(Na)_2(s) + Ca^{2+}(aq) \rightarrow resin\text{-}Ca(s) + 2Na^+(aq)$

$resin\text{-}(Na)_2(s) + Mg^{2+}(aq) \rightarrow resin\text{-}Mg(s) + 2Na^+(aq)$

The ion exchange resin must be 'regenerated' at regular intervals by passing a concentrated solution of sodium chloride through it and discarding the calcium (and magnesium) rich water that is produced.

$resin\text{-}Ca(s) + 2Na^+(aq) \rightarrow resin\text{-}(Na)_2(s) + Ca^{2+}(aq)$

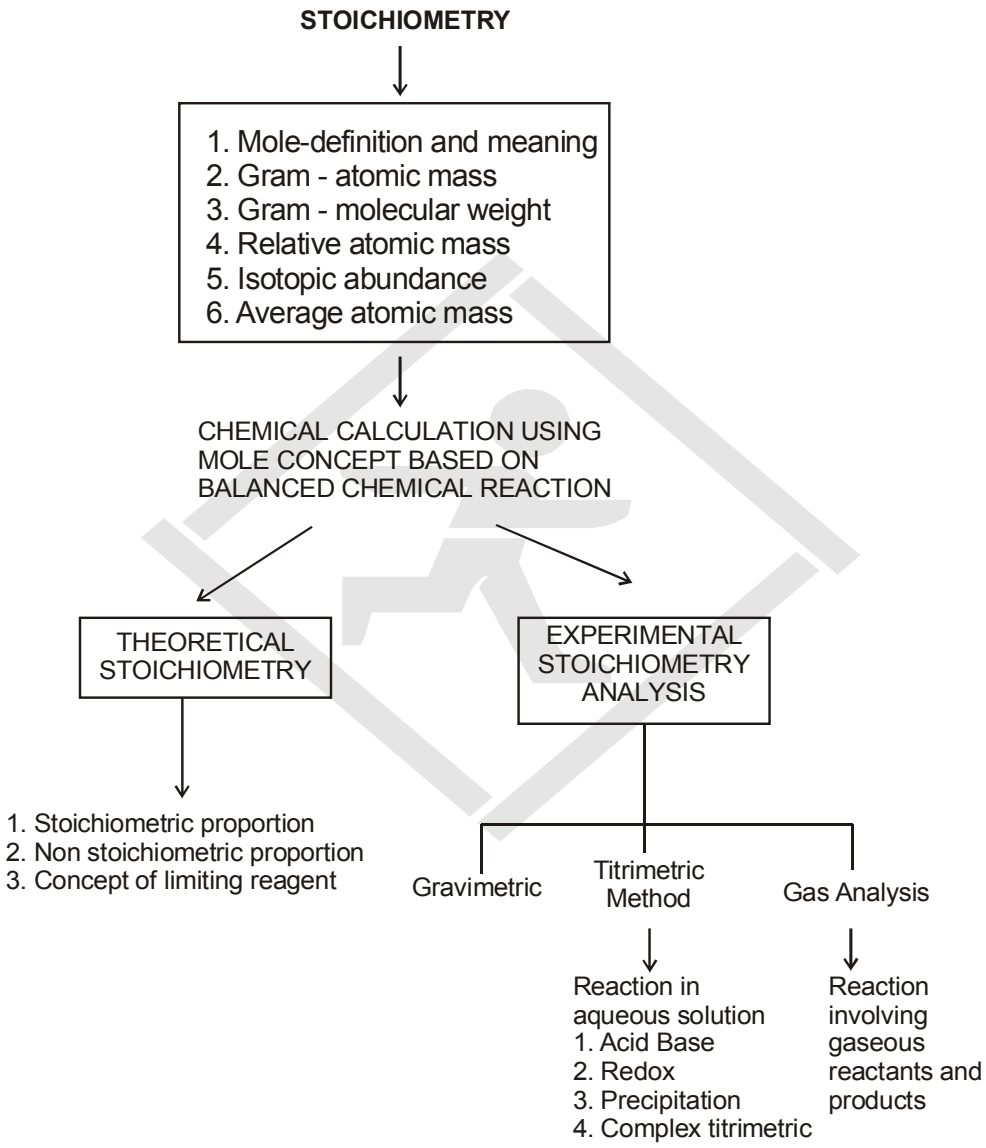


4. Removal of permanent hardness by complexation

The sodium salts of chain polyphosphates are able to complex with calcium and magnesium ions thus preventing them from forming a scum with soap.

$Ca^{2+}(aq) + P_3O_{10}^{5-}(aq) \rightarrow CaP_3O_{10}^{3-}(aq)$

THE ATLAS



GLOSSARY

Aliquot . A portion of the whole, usually a simple fraction. A portion of a sample withdraw from a volumetric flask with a pipet is called as aliquot.

Analytical concentration, The total number of moles per litre of a solute regardless of any reactions that might occur when the solute dissolves. Used synonymously with formality.

Equivalent. The amount of a substance which furnishes or reacts with 1 mole of H^+ (acid-base), 1 mol of electrons (redox), or 1 mol of a univalent cation (precipitation and complex formation).

Equivalent weight. The weight in grams of one equivalent of a substance.

Equivalence point. The point in a titration where the number of equivalents of titrant is the same as the number of equivalents of analyte.

End point. The point in a titration where an indicator changes color.

Formula weight. The number of formula weights of all the atoms in the chemical formula of a substance.

Formality. The number formula weights of solute per litre of solution; synonymous with analytical concentration.

Indicator. A chemical substance which exhibits different colors in the presence of excess analyte or titrant.

Normality. The number of equivalents of solute per litre of solution.

Primary standard. A substance available in a pure form or state of known purity which is used in standardizing a solution.

Standardization. The process by which the concentration of a solution is accurately ascertained.

Standard solution. A solution whose concentration has been accurately determined.

Titrant. The reagent (a standard solution) which is added from a buret to react with the analyte.

SOLVED OBJECTIVE

OXIDATION REDUCTION

Ex.1 Which of the following acts as both oxidant and reductant –

(A) HNO_3 (B) HNO_2 (C) Both HNO_3 & HNO_2 (D) Neither HNO_3 nor HNO_2

Ans. **B**

Sol. O.N. of N in HNO_2 is +3

Max. O.N. of N is +5

Min. O.N. of N is –3

Thus O.N. of N in HNO_2 can show an increase or decrease as the case may be. That is why HNO_2 acts as oxidant and reductant both.

O.N. of N in HNO_3 is +5, Hence it can act only as an oxidant.

Ex.2 State which of the following reactions is neither oxidation nor reduction –

(A) $Na \rightarrow NaOH$ (B) $Cl_2 \rightarrow Cl^- + ClO^-_3$ (C) $P_2O_5 \rightarrow H_4P_2O_7$ (D) $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$

Ans. **C**

Sol. In the reaction $P_2O_5 \rightarrow H_4P_2O_7$

The O.N. of P in P_2O_5 is

$2x + 5 (-2) = 0$ or $x = +5$

The O.N. of P in $H_4P_2O_7$ is

$4 (+1) + 2 (x) + 7 (-2) = 0$

$2x = 10$ or $x = +5$

Since there is no change in O.N. of P, hence the above reaction is neither oxidation nor reduction.

Ex.3 In the reaction

$C_2O_4^{-2} + MnO^-_4 + H^+ \rightarrow Mn^{+2} + CO_2$

the reductants is –

(A) $C_2O_4^{-2}$ (B) H^+ (C) MnO^-_4 (D) None of the above

Ans. **A**

Sol. In the above reaction $C_2O_4^{-2}$ acts as a reductant because it is oxidised to CO_2 as :

$C_2O_4^{-2} \rightarrow 2CO_2 + 2e$(oxidation)

$C_2O_4^{-2}$ reduces MnO_4^- to Mn^{+2} ion in solution.

Ex.4 The order of increasing O.N. of S in S_8, $S_2O_8^{-2}$, $S_2O_3^{-2}$, $S_4O_6^{-2}$ is given below –

(A) $S_8 < S_2O_8^{-2} < S_2O_3^{-2} < S_4O_6^{-2}$ (B) $S_2O_8^{-2} < S_2O_3^{-2} < S_4O_6^{-2} < S_8$

(C) $S_2O_8^{-2} < S_8 < S_4O_6^{-2} < S_2O_3^{-2}$ (D) $S_8 < S_2O_3^{-2} < S_4O_6^{-2} < S_2O_8^{-2}$

Ans. **D**

Sol. The O.Ns. of S are shown below along with the compounds

S_8,	$S_2O_8^{-2}$,	$S_2O_3^{-2}$,	$S_4O_6^{-2}$
0	+ 6	+2	+2.5

Hence the order of increasing O.N. of S is

$S_8 < S_2O_3^{-2} < S_4O_6^{-2} < S_2O_8^{-2}$

Ex.5 The composition of a sample of wustite is $Fe_{0.93}O_{1.00}$. What percentage of iron is present in the form of Fe(III)

(A) 13.05 (B) 14.05 (C) 15.05 (D) 16.05

Ans. **C**

Sol. O.N. of. Fe in wustite is = $\frac{200}{93}$ = 2.15

It is an intermediate value in between Fe (II) & Fe (III)

Let % of Fe (III) be a, then

$2 \times (100 - a) + 3 \times a = 2.15 \times 100$

$a = 15.05$

$\therefore$ % of Fe (III) = 15.05%

Ex.6 The oxid.no. of Cl in $NOClO_4$ is –

(A) + 11 (B) + 9 (C) + 7 (D) + 5

Ans. **C**

Sol. The compound may be written as $NO^+ ClO_4^-$

For ClO_4^-, Let Ox. No.of Cl = a

$a + 4 \times (-2) = -1$

$a = +7$

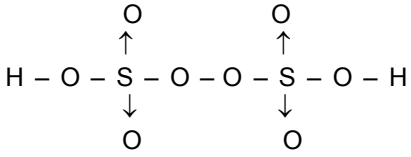
Hence, the oxidation no. of Cl in $NOClO_4$ is +7.

Ex.7 The oxidation number of S in $H_2S_2O_8$ is –

(A) +8 (B) –8 (C) +6 (D) +4

Ans. **C**

Sol. In $H_2S_2O_8$, two O atoms form peroxide linkage i.e.



$2 \times 1 + 2a + 6(-2) + 2(-1) = 0$

$\therefore \quad a = +6$

Thus the O.N. of S in $H_2S_2O_8$ is + 6

Ex.8 In the reaction $Al + Fe_3O_4 \rightarrow Al_2O_3 + Fe$ –
what is the total no. of electrons transferred during the change –

(A) 16 (B) 24 (C) 8 (D) 12

Ans. **B**

Sol. $2Al^{o} \rightarrow Al_2^{+3} + 6e^{-}$ ..... (A)

$8e + Fe_3^{+8/3} \rightarrow 3Fe^{o}$ ..... (B)

Multiplying Eq. (A) by 4 and Eq. (B) by 3, then on addition

$8Al^{o} \rightarrow 4Al_2^{+3} + 24e$

$24e + 3Fe_3^{+8/3} \rightarrow 9Fe^{o}$

$8Al^{o} + 3Fe_3^{+8/3} \rightarrow 9Fe^{o} + 4Al_2^{+3}$

or $8Al + 3Fe_3O_4 \rightarrow 4Al_2O_3 + 9Fe$

Therefore, it is clear that total no. of electrons transferred during change = 24

Ex.9 In the redox reaction –

$10FeC_2O_4 + x\,KMnO_4 + 24H_2SO_4 \rightarrow$

$5Fe_2(SO_4)_3 + 20CO_2 + y\,MnSO_4 + 3\,K_2SO_4 + 24H_2O.$

The values of x and y are respectively –

(A) 6, 3 (B) 3, 6 (C) 3, 3 (D) 6, 6

Ans. **D**

Sol. The balanced redox reaction given above can be written as :

$10FeC_2O_4 + 6KMnO_4 + 24H_2SO_4 \rightarrow$

$5Fe_2(SO_4)_3 + 20CO_2 + 6\,MnSO_4 + 3\,K_2SO_4 + 24H_2O$

so the value of x = 6 and y = 6

Ex.10 Which of the following is correctly balanced half reaction –

(A) $AsO_3^{-3} + H_2O \rightarrow AsO_4^{-3} + 2H^{+} - 2e^{-}$ (B) $H_2O_2 + 2e \rightarrow O_2 + 2H^{+}$

(C) $Cr_2O_7^{-2} + 14H^{+} \rightarrow 2Cr^{+3} + 7H_2O - 6e^{-}$ (D) $IO^{-}_3 + 6H^{+} \rightarrow I_2 + 3H_2O + 5e^{-}$

Ans. **C**

Sol. The correctly balanced half reaction is –

$Cr_2O_7^{-2} + 14H^{+} \rightarrow 2Cr^{+3} + 7H_2O - 6e^{-}$ It is a reduction half reaction in balancing the equation by ion–electron method.

EQUIVALENT CONCEPT

Ex.1 In the reaction

$Br_2 + Na_2CO_3 \longrightarrow NaBr + NaBrO_3 + CO_2$

The equiv. wt. of $NaBrO_3$ is

(A) $\frac{\text{Mol. wt}}{1}$ (B) $\frac{\text{Mol. wt}}{10}$ (C) $\frac{\text{Mol. wt}}{5}$ (D) $\frac{\text{Mol. wt}}{4}$

Sol. Per mole of the formation
$NaBrO_3$ the x factor = + 5

$\therefore$ equiv. wt. of $NaBrO_3 = \frac{\text{Mol. wt}}{5}$

Ans. **C**

Ex.2 The equiv. wt. of hypo in the reaction
$Na_2S_2O_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + H_2SO_4 + HCl$ is –

(A) $\frac{\text{Mol. wt}}{2}$ (B) $\frac{\text{Mol. wt}}{4}$ (C) $\frac{\text{Mol. wt}}{1}$ (D) $\frac{\text{Mol. wt}}{8}$

Sol. $Na_2\overset{+2}{S_2}O_3 + Cl_2 + H_2O \longrightarrow Na_2\overset{+6}{S}O_4 + H_2\overset{+6}{S}O_4 + HCl$

$\therefore$ x factor for $Na_2S_2O_3 = 2|(2 - 6)| = 8$

$\therefore$ equiv. wt. of $Na_2S_2O_3 = \frac{\text{Mol. wt}}{8}$

Ans. **D**

Ex.3 In acting as a reducing agent, a piece of metal M weighing 16 grams gives up 2.25×10^{23} electrons, what is the equiv.alent weight of the metal

(A) 42.83 (B) 21.33 (C) 83.32 (D) 32

Sol. N_A no of electron will be removed by

$\frac{6.023 \times 10^{23}}{2.25 \times 10^{23}}$ × 16 gm of metal M

= 42.83 gm of metal M

$\therefore$ equiv. wt. of metal is 42.83

Ans. **A**

Ex.4 What weight of HNO_3 is needed to convert 62 gm of P_4 in H_3PO_4 in the reaction ?
$P_4 + HNO_3 \longrightarrow H_3PO_4 + NO_2 + H_2O$

(A) 63 gm (B) 630 gm (C) 315 gm (D) 126 gm

Sol. The equiv. wt. of $P_4 = \frac{31 \times 4}{5 \times 4} = \frac{31}{5}$

$\therefore$ 62 gm $P_4 = \frac{62 \times 5}{31}$ equiv. of P_4 = 10 equiv. of P_4

The equiv. wt. of $HNO_3 = \frac{\text{Mol. wt}}{1} = \frac{63}{1}$

$\therefore$ the wt. of HNO_3 required = 10 × 63 = 630 gm

Ans. **B**

Ex.5 The equiv. wt. of an element is 9. If it forms volatile chloride of vapour density 58.5. What is the approximate at wt. of the element ?

(A) 9 (B) 18 (C) 27 (D) 54

Sol. Let, the molecular formula of the chloride is MCl_x and at wt. of the element is a
$9x + x \times 35.5 = 58.5 \times 2$

$x = \frac{58.5 \times 2}{44.5} = 2.63$

The nearest whole no. of 2.63 = 3
approximate at wt. of the element = 9 × 3 = 27

Ans. C

Ex.6 500 ml of 0.2 (M) H_2SO_4 are mixed with 250 ml of 0.1 (M) $Ba(OH)_2$, the normality of resulting solution is -
(A) 0.2 (B) 0.1 (C) 0.5 (D) 0.25

Sol. 500 ml of 0.2 (M) H_2SO_4 = 500 × 0.2 × 10^{-3} moles of H_2SO_4
= 0.5 × 0.2 × 2 equiv. of H_2SO_4 = 0.2 equiv. of H_2SO_4
250 ml of 0.1 (M) $Ba(OH)_2$, = 250 × 0.1 × 10^{-3} moles of Ba $(OH)_2$
= 250 × 0.1 × 10^{-3} × 2 = 0.05 equiv. of Ba $(OH)_2$
∴ Excess H_2SO_4 = 0.2 – 0.05 = 0.15 equiv.

Hence normality of H_2SO_4 in resulting solution = $\frac{0.15}{750}$ × 1000 = 0.2 (N)

Ans. **A**

Ex.7 What weight of $H_2C_2O_4$, $2H_2O$ (mol. wt. = 126) should be dissolved to prepare 250 ml of centinormal to be used as a reducing agent ?
(A) 0.63 gm (B) 0.1575 gm (C) 0.126 gm (D) 0.875 gm

Sol. Per mole of given acid $C_2O_4^{2-}$ present
= 1 mole
∴ $C_2O_4^{2-} \longrightarrow CO_2 + 2e$
∴ x factor for $H_2C_2O_4$, $2H_2O$ as a reducing agent = 2

∴ equiv. wt. = $\frac{126}{2}$ = 63

250 ml of seminormal solution = $\frac{250}{100}$ × 10^{-3} equiv.

∴ wt. of $H_2C_2O_4$, $2H_2O$ required = $\frac{250}{100}$ × 10^{-3} × 63 gm = 0.1575 gm

Ans. **B**

Ex.8 Which of the following has the highest normality ? (consider each of the acid is 100% ionised.)
(A) 1 (M) H_2SO_4 (B) 1 (M) H_3PO_3 (C) 1 (M) H_3PO_4 (D) 1 (M) HNO_3

Sol. The normality of 1(M) H_2SO_4 = 2(N)
The normality of 1(M) H_3PO_3 = 2(N)
The normality of 1(M) H_3PO_4 = 3(N)
The normality of 1(M) HNO_3 = 1(N)

Ans. **C**

Ex.9 0.45 gm of an acid of mol. wt. 90 was neutralised by 20 ml of 0.5 (N) caustic potash. The basicity of acid is-
(A) 1 (B) 2 (C) 3 (D) 4

Sol. 20 ml of 0.5 (N) caustic potash
= 20 × 0.5 × 10^{-3} equiv. of caustic potash
∴ 20 × 0.5 × 10^{-3} equiv. of acid = 0.45 gm

∴ 1 equiv. of acid = $\frac{0.45}{10 \times 10^{-3}}$ = 45 gm

∴ x for acid = $\frac{90}{45}$ = 2
Hence, basicity of acid = 2

Ans. **B**

Ex.10 The equivalent wt. of a metal is double that of oxygen. How many times is weight of its oxide greater than the wt. of metal ?
(A) 2 (B) 3 (C) 1.5 (D) 0.25

Sol. The equiv. wt. of the metal = 16
The equiv. wt. of the metal oxide = 16 + 8 = 24

∴ oxide is $\frac{24}{16}$ = 1.5 times greater than the wt. of metal

Ans. **C**

SOLVED SUBJECTIVE

1. 0.24 gm of metal is dissolved completely in excess of dil. H_2SO_4 solution. If 82.5 ml dry hydrogen gas is liberated at 27°C and cm Hg, what is the equivalent weight of the metal ?

Sol: From ideal gas equation, PV=nRT

$$\frac{95}{76}\times\frac{82.5}{1000}=\frac{w}{2}=0.082\times300$$

Weight of hydrogen gas liberated out, $w=8.38\times10^{-3}$ gm

$\therefore$ 8.38×10^{-3} gm hydrogen is liberated from 0.24 gm mtal

$\therefore$ 1 gm hydrgoen will be liberated from $\frac{0.24}{8.38\times10^{-3}}\times1 = 28.64$ gm

Equivalent weight of metal = **28.64.**

2. metal oxide contains 47% oxygen by weight. Determine the equivalent weight of metal.

Sol. If we take 100 gm of oxide, it contains 47 gm oxygen and hence rest, 53 gm metal

Now, No. of g-eq. of metal=no. of g-eq. of oxygesn

$$\text{or, } \left(\frac{W}{E}\right)_{metal}=\left(\frac{W}{E}\right)_{oxygen}$$

$$\text{or, } \frac{53}{E}=\frac{47}{8}$$

$\therefore$ Equivalent weight of metal, E=**9.02**

3. 4.0 g of monobasic, saturated carboxylic acid is dissolved in 100 mL water and its 10 mL portion required 8.0 mL 0.27 M NaOH to reach the equivalence point. In an another experiment, 5.0 g of the same acid is burnt completely and CO_2 produced is absorbed completely in 500 mL of a 2.0 N NaOH solution. A 10 mL portion of the resulting solution is treated with excess of $BaCl_2$ to precipitate all carbonate and finally titrated with 0.5 N H_2SO_4 solution. Determine the volume of the acid solution that would be required to make this solution neutral.

Sol. meq. of NaOH = 8 × 0.27 = meq. of acid for 10 ml of acid solution

$$\text{meq. of acid for 100 ml of solution} = \frac{8\times0.27\times100}{10} = \frac{4}{M}\times10^3$$

$$M\text{ (acid)} = \frac{4}{8\times0.27\times10}\times1000 = 185.2$$

Formula of acid. = $C_nH_{2n}O_2$

$\Rightarrow$ M = 14n + 32 = 185.2

$\Rightarrow$ n = 11

Now 5g acid will produce $\frac{5}{185.2}\times11 = \frac{55}{185.2}$ mol CO_2 after complete combustion.

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

Total mass of NaOH available = $500\times2\times10^{-3}$ = 1.0 mole

Moles of NaOH left unreacted = $1-\frac{2\times55}{185.2} = \frac{76}{185.2}$ in 500 mL

$\Rightarrow$ Molarity of NaOH after precipitation of Na_2CO_3 = 0.812

Therefore, 0.812 × 10 = 0.5 × V

$\Rightarrow$ V = 16.24 mL **Ans.**

4. 2.5 g of a mixture containing $CaCO_3$, $Ca(HCO_3)_2$ and NaCl was dissolved in 100 mL water and its 10 mL portion required 10 mL 0.05 M H_2SO_4 solution to reach the phenolphthalein end point. An another 10 mL portion of the same stock solution required 32.35 mL of the same acid solution to reach the methyl orange end point. Determine mass percentage of $CaCO_3$ and $Ca(HCO_3)_2$ in the original mixture.

Sol. Let a and b are the meq. of $CaCO_3$ and $Ca(HCO_3)_2$ respectively.
When HPh is used is indicater then only $CaCO_3$ will react with H_2SO_4
$H_2SO_4+CaCO_3 \rightarrow Ca(HSO_4)_2+H_2CO_3$
meq. of H_2SO_4 = 1/2 meq. of $CaCO_3$

meq. of $H_2SO_4 = \frac{10 \times 0.05 \times 100 \times 2}{10}$ = 10, meq. of $CaCO_3$ = 20

When MeOH is used as indicator
$Ca(HCO_3)_2+H_2SO_4 \rightarrow CaSO_4 + H_2CO_3$
$CaCO_3+H_2SO_4 \rightarrow H_2CO_3+CaSO_4$
then meq. of $CaCO_3$ + meq. of $Ca(HCO_3)_2$ = meq. of H_2SO_4

$a + b = \frac{32.35 \times 0.05 \times 2}{10} \times 100$, $a + b = 32.35$, $b = 12.5$

wt. of $CaCO_3 = a \times 10^{-3} \times 100/2 = 1$ gm
wt. of $Ca(HCO_3)_2 = b \times 10^{-3} \times 162/2 = 1$ gm

% of $CaCO_3 = \frac{1}{2.5} \times 100 = 40\%$, % of $Ca(HCO_3)_2 = \frac{1}{2.5} \times 100 = 40\%$

5. 6.4 g of a pure monobasic organic acid is burnt completely in excess of oxygen and CO_2 evolved is absorbed completely in one litre of an aqueous solution of NaOH. A 10 mL portion of this solution required 14.5 mL of a normal HCl solution to reach the phenolphthalein end point. An another 10 mL portion of the same solution required 18 mL of the same HCl solution to reach the methyl organe end point. If the organic acid contains 25% oxygen by weight, deduce the empirical formula of this acid and strength of original NaOH solution.

Sol. $C_xH_yO_2 + O_2 \rightarrow xCO_2 \xrightarrow{2NaOH} xNa_2CO_3$

$\frac{6.4}{M}$ $\frac{6.4x}{M}$ $\frac{6.4x}{M}$

Let 100 ml of solution contains a meq. of NaOH & b meq. of Na_2CO_3
when HPh is used as indicator then

meq. of NaOH + 1/2 meq. of Na_2CO_3 = Meq. of HCl, = $\frac{14.5 \times 1}{10} \times 1000 = 40\%$,

$a + b/2 = 14.5 \times 100 = 1450$ ...(1)
when MeOH is used as indicator, meq. of NaOH + meq. of Na_2CO_3 = Meq. of HCl

$a + b = 18 \times 1 \times \frac{1}{10} \times 100 = 1800$ ...(2), from (1) & (2)

b = 700, a = 100, moles of $Na_2CO_3 = \frac{b \times 10^{-3}}{2} = \frac{6.4}{M} \times x$

$\Rightarrow \frac{700 \times 10^{-3}}{2} = 6.4 \frac{x}{M}$ ...(1), wt % of = 25

$M \times \frac{25}{100} = 32 \Rightarrow M = 128$,

from (1) $\frac{700\times10^{-3}}{2} = 6.4 \times \frac{x}{128}$

$\frac{700\times10^{-3}}{2} \times \frac{128}{6.4} = x = 7$

formula $C_7H_{12}O_2$

Molarity of NaOH = $\frac{1800}{1000}$ = 1.8 M **Ans.**

6. A solution contains Na_2CO_3 and $NaHCO_3$. 10 mL of the solution requires 2.5 mL of 0.1 M H_2SO_4 for neutralisation using phenolphthalein as an indicator. Methyl organge is added when a further 2.5 mL of 0.2 M H_2SO_4 was required. Calculate the amount of Na_2CO_3 and $NaHCO_3$ in one litre of the solution.

Sol. Na_2CO_3 $NaHCO_3$

Let a meq. b meq.

when HPh is used as indicator

$Na_2CO_3+H_2SO_4 \rightarrow NaHCO_3+NaHSO_4$

then $\frac{1}{2}$ meq. of Na_2Cl_3 = meq. of H_2SO_4

$$\frac{a}{2} = 2.5 \times 0.1 \times 2 \Rightarrow a = 1$$

MeOH is added after the first end point the solution

Contains $NaHCO_3$ original & $NaHCO_3$ produced.

$NaHCO_3+H_2SO_4 \rightarrow H_2CO_3+NaHSO_4$

meq. of H_2SO_4 = meq. of $NaHCO_3$ original + meq. of $NaHCO_3$ produced

$2.5 \times 0.2 \times 2 = b + 1/2$ meq. of Na_2CO_3

$= b + a/2$

$b + a/2 = 1$

$b = 1 - 0.5 = 0.5$

wt of Na_2CO_3/lit = $a \times 10^{-3} \times \frac{106}{2} \times \frac{1}{10} \times 1000$

$= 1 \times \frac{53}{10} = 5.3$ gm

wt of $NaHCO_3$/lit = $b \times 10^{-3} \times 84 \times \frac{1}{10} \times 1000 = 4.2$ gm **Ans.**

7. A 2.0 g sample of a mixture containing sodium carbonate , sodium bicarbonate and sodium sulphate is heated till the evolution of CO_2 ceases.The volume of CO_2 at 750 mm Hg pressure and at 298 K is measured to be 123. 9 mL. A 1.5 g of the sample requires 150 mL of M/10 HCl for complete neutralization . Calculate the percentage composition of the components of the mixture.

Sol. Out of Na_2CO_3, $NaHCO_3$ and Na_2SO_4 only $NaHCO_3$ decomposes on heating to give CO_2 gas, according to the equation $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$

moles of CO_2 = $\frac{PV}{RT} = \frac{750x123.9}{760 \text{ x } 1000 \text{ x } 0.082 \text{ x } 298} = 5 \text{ x } 10^{-3}$

$\therefore$ moles of $NaHCO_3$ = 2 x 5 x 10^{-3} = 0.01

Equivalents of HCl used $= \frac{150 \times \frac{1}{10}}{1000} = 1.5 \times 10^{-2}$

Equivalents of $NaHCO_3$ in 1.5 g = 0.01 x $\frac{1.5}{2}$ = 7.5 x 10^{-3}

$\therefore$ Equivalents of Na_2CO_3 = 1. 5 x 10^{-2} - 7. 5 x 10^{-3} = 7. 5 x 10^{-3}

Moles of Na_2CO_3 = $\frac{7.5 \times 10^{-3}}{2}$ (when Na_2CO_3 reacts with HCl it gives NaCl, CO_2 and H_2O .No atom undegoes change in oxidation state . $\therefore$ 'n' factor of Na_2CO_3 = 2) = 3.75 x 10^{-3}

Mass of $NaHCO_3$ in 1. 5 g = 7. 5 x 10^{-3} x 84 = 0.63 g

Mass of Na_2CO_3 in 1.5 g = 3.75 x 10^{-3} x 106 = 0.3975 g

$\therefore$ mass of Na_2SO_4 = 1.5 - 0.63 - 0.3975 = 0.4725 g.

Percentage of $NaHCO_3 = \frac{0.63}{1.5} \times 100 = 42\%$

Percentage of Na_2CO_3 = $\frac{0.3975}{1.5} \times 100 = 26.5\%$

Percentage of Na_2SO_4 = $\frac{0.4725}{1.5} \times 100 = 31.5\%$

8. A 1. 0 g sample of Fe_2O_3 solid of 55. 2 % purity is dissolved in acid and reduced by heating the solution with zinc dust. The resultant solution is cooled and made upto 100. 0 mL. An aliquot of 25. 0 mL of this solution requires 17. 0 mL of 0.0167 M solution of an oxidant for titration. Calculate the number of electrons taken up by the oxidant in the reaction of the above titration.

Sol. Mass of $Fe_2O_3 = \frac{55.2}{100} \times 1 = 0.552g$

moles of $Fe_2O_3 = \frac{0.552}{160} = 3.45 \times 10^{-3}$

Equivalents of the oxidant $= \frac{n \times 0.0167 \times 17}{1000} = 2.84 \times 10^{-4} n$

(n is the 'n' factor of the oxidant)

Since on adding Zinc dust to the Fe_2O_3 solution all the Fe^{+3} will become Fe^{+2} , moles of Fe^{2+} in 100 mL = 3.45 x 10^{-3} x 2 = 6. 9 x 10^{-3}

$\therefore$ Equivalents of Fe^{2+} in the 25 mL that is reacting with oxidant $= \frac{6.9 \times 10^{-3}}{4} = 1.725 \times 10^{-3}$

$\therefore$ according to the Law of Equivalents = 1. 725 x 10^{-3} = 2.84 x 10^{-4} n

$\therefore n = \frac{1.725 \times 10^{-3}}{2.84 \times 10^{-4}} = 6.07 \approx 6$

9. A 8. 0 g sample contained Fe_3O_4, Fe_2O_3 and inert materials . It was treated with an excess of aqueous KI Solution in acidic medium,which reduced all the iron to Fe^{+2} ions. The resulting solution was diluted to 50.0 cm^3 and a 10. 0 cm^3 of it was taken. The liberated iodine in this

solution required 7. 2 cm³ of 1. 0 M $Na_2S_2O_3$ for reduction to iodide . The iodine from another 25. 0 cm³ sample was extracted , after which the Fe^{+2} ions was titrated against 1. 0 M MnO_4^- in acidic medium . The volume of $KMnO_4$ solution used was found to be 4. 2 cm³. Calculate the mass percentages of Fe_3O_4 andof Fe_2O_3 in the original mixture.

Sol. This problem can be done by two methods.

In the first method, we break up Fe_3O_4 as an equimolar mixture of FeO and Fe_2O_3

Method (1)

Fe_3O_4 is FeO. Fe_2O_3

Equivalents of $Na_2S_2O_3$ = $\frac{1 \text{ x } 7.2}{1000} = 7.2 \text{ x } 10^{-3}$

Equivalents of I_2 in 10 cc = 7. 2 x 10^{-3}

Equivalents of I_2 in 50 cc = 7 . 2 x 10^{-3} x 5 = 3.6 x 10^{-2}

Since equivalents of I_2 is equal to that of KI which in turn is equal to the total equivalents of Fe_2O_3 (Fe_2O_3 in the free state and Fe_2O_3 combined with FeO)

$\therefore$ equivalents of total Fe_2O_3 = 3. 6 x 10^{-2}

Equivalents of $KMnO_4$ solution = $\frac{4.2 \text{ x } 1 \text{ x } 5}{1000} = 2.1 \text{ x } 10^{-2}$

Since $KMnO_4$ reacts with the total Fe^{2+} (Fe^{2+} in FeO and Fe^{2+} that was produced by the action of KI on Fe_2O_3)

$\therefore$ equivalents of total Fe^{2+} in 50 ml = 2.1 x 10^{-2} x 2 = 4.2 x 10^{-2}

Since equivalent of Fe^{2+} produced from Fe_2O_3 is equal to that of equivalents of Fe_2O_3

$\therefore$ Equivalents of FeO = 4.2 x 10^{-2} - 3.6 x 10^{-2} = 6 x 10^{-3}

$\therefore$ moles of FeO = 6 x 10^{-3}

moles of Fe_2O_3 combined with FeO = 6 x 10^{-3}

total moles of Fe_2O_3 = $\frac{3.6 \text{ x } 10^{-2}}{2}$

(because when $Fe_2O_3 \rightarrow Fe^{2+}$ 'n' factor is 2). = 1.8 x 10^{-2}

moles of Fe_2O_3 in the free state = 1.8 x 10^{-2} - 6 x 10^{-3} = 1. 2 x 10^{-2}

mass of Fe_3O_4 = 6 x 10^{-3} x 232 = 1.392 g

mass of Fe_3O_4 = 1. 2 x 10^{-2} x 160 = 1.92 g

percentage Fe_2O_4 = 17.4 %

percentage of Fe_2O_3 = 23. 75 %

Method 2 :

Here we take Fe_3O_4 as a single entity.

Equivalents of $Na_2S_2O_3$ = $\frac{7.2 \text{ x } 1}{1000} = 7.2 \text{x} 10^{-3}$

Equivalents of I_2 in 50 cc = 7. 2 x 10^{-3} x 5 = 3.6 x 10^{-2}

$\therefore$ Equivalents of Fe_3O_4 + Fe_2O_3 = 3. 6 x 10^{-2}

Let us assume that the moles of Fe_3O_4 is x g and that of Fe_2O_3 is y g .

Since on reacting with KI both Fe_3O_4 and Fe_2O_3 give Fe^{2+} 'n' factor for both is two.

$\therefore$ 2x + 2y = 3.6 x 10^{-2} ---------- (1)

Equivalents of $KMnO_4$ = $\frac{4.2 \text{ x } 1 \text{ x } 5}{1000} = 2.1 \text{ x } 10^{-2}$

moles of Fe^{2+} in 50 mL = 4. 2 x 10^{-2}

Since the moles of Fe_3O_4 are x, moles of Fe^{2+} produced from Fe_3O_4 will be 3x and that produced from Fe_2O_3 will be 2y

$\therefore$ 3x + 2y = 4. 2 x 10-2 --------- (2)
(2) - (1) gives x = 6 x 10^{-3}
$\therefore$ y = 1.2 x 10^{-2}
Solving this percentage of Fe_3O_4 is 17.4 % and Fe_2O_3 is 23.75 %

10. A solution contains Na_2CO_3 and $NaHCO_3$. 20 cm³ of this solution requires 5. 0 cm³ of 0.1 M H_2SO_4 Solution for neutralization using phenolphthalein as the indicator .Methylorange is then added when a further 5.0 cm³ of 0.2 M H_2SO_4 was required . Calculate the masses of Na_2CO_3 and $NaHCO_3$ is 1L of this solution.

Solution : $Na_2CO_3 + \frac{1}{2}H_2SO_4 \rightarrow NaHCO_3 + \frac{1}{2}Na_2SO_4$

phenolphthalein would change the colour after this reaction.
Meq. of H_2SO_4 used for 5 ml mixture using phenolpthalein as indicator.
= 2 x 0.1 x 5 = 1

$\therefore \frac{1}{2}$ Meq. of Na_2CO_3 = 1

Now methyl orange is added in this solution after 1 end point.
Meq. of H_2SO_4 used for solution after 1 end point using methyl orange as Indicator = 5 x 0. 2 x 2 = 2

$\therefore \frac{1}{2}$ Meq. of Na_2O_3 + Meq . of $NaHCO_3$ = 2

Meq. of $NaHCO_3$ = 2 -1 = 1

$\frac{W}{84} x 1000 = 1$ $\therefore$ W = 0.084 g

$\therefore$ Weight of $NaHCO_3$ in one litre $= \frac{0.084 x 1000}{20} = 4.2g$

$\therefore$ Meq. of Na_2CO_3 = 2 $\therefore \frac{W}{53} x 1000 = 2$

or $W = \frac{106}{1000} = 0.106$

$\therefore$ Weight of $NaHCO_3$ in 1litre $\frac{0.106}{20} x\ 1000 = 5.3g$

SOLVED EXAMPLE
IIT-JEE MAIN

Ex.1 In the reaction

$Br_2 + Na_2CO_3 \longrightarrow NaBr + NaBrO_3 + CO_2$

The equiv. wt. of $NaBrO_3$ is

(A) $\frac{\text{Mol.wt}}{1}$ (B) $\frac{\text{Mol.wt}}{10}$ (C) $\frac{\text{Mol.wt}}{5}$ (D) $\frac{\text{Mol.wt}}{4}$

(Ans.C)

Sol. x-factor for formation of $NaBrO_3$ = + 5

$\therefore$ Equiv. wt. of $NaBrO_3 = \frac{\text{Mol.wt}}{5}$

Ex.2 The equiv. wt. of hypo in the reaction

$Na_2S_2O_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + H_2SO_4 + HCl$ is –

(A) $\frac{\text{Mol.wt}}{2}$ (B) $\frac{\text{Mol.wt}}{4}$ (C) $\frac{\text{Mol.wt}}{1}$ (D) $\frac{\text{Mol.wt}}{8}$

(Ans. D)

Sol. $Na_2\overset{+2}{S_2}O_3 + Cl_2 + H_2O \longrightarrow Na_2\overset{+6}{S}O_4 + H_2\overset{+6}{S}O_4 + HCl$

$\therefore$ x factor for $Na_2S_2O_3 = 2|(2 - 6)| = 8$

$\therefore$ equiv. wt. of $Na_2S_2O_3 = \frac{\text{Mol.wt}}{8}$

Ex.3 In acting as a reducing agent, a piece of metal M weighing 16 grams gives up 2.25×10^{23} electrons, what is the equivalent weight of the metal

(A) 42.83 (B) 21.33 (C) 83.32 (D) 32

(Ans. A)

Sol. N_A electron will be removed by

$\frac{6.023\times10^{23}}{2.25\times10^{23}}$ × 16 gm of metal M

= 42.83 gm of metal M

$\therefore$ equiv. wt. of metal is 42.83

Ex.4 The equiv. wt. of the salt $KHC_2O_4.H_2C_2O_4.4H_2O$ (to be used as a reducing agent) is -

(A) $\frac{\text{Mol.wt}}{1}$ (B) $\frac{\text{Mol.wt}}{2}$ (C) $\frac{\text{Mol.wt}}{3}$ (D) $\frac{\text{Mol.wt}}{4}$

(Ans. D)

Sol. Per moles of this salt, moles of $C_2O_4^{2-} = 2$

$\therefore$ no of electrons transferred per moles of this salt is

$2C_2O_4^{2-} \longrightarrow 2 \times 2e = 2CO_2 \times 2$

$\therefore$ x' factor(as a reducing) of the given salt =4

$\therefore$ equiv. wt. of the given salt = $\frac{\text{Mol.wt}}{4}$

Ex.5 What weight of HNO_3 is needed to convert 62 gm of P_4 in H_3PO_4 in the reaction ?
$P_4 + HNO_3 \longrightarrow H_3PO_4 + NO_2 + H_2O$
(A) 63 gm (B) 630 gm (C) 315 gm (D) 126 gm

(Ans. B)

Sol. The equiv. wt. of $P_4 = \frac{31\times4}{5\times4} = \frac{31}{5}$

$\therefore$ 62 gm $P_4 = \frac{62\times5}{31}$ equiv. of P_4 = 10 equiv. of P_4

The equiv. wt. of $HNO_3 = \frac{\text{Mol.wt}}{1} = \frac{63}{1}$

$\therefore$ the wt. of HNO_3 required
$= 10 \times 63 = 630$ gm

Ex.6 The equiv. wt. of an element is 9. If it forms volatile chloride of vapour density 58.5. What is the approximate at wt. of the element ?
(A) 9 (B) 18 (C) 27 (D) 54

(Ans. C)

Sol. Let, the molecular formula of the chloride is MCl_x and at wt. of the element is a
$\therefore 9x + x \times 35.5 = 58.5 \times 2$ (E = a/x)

$x = \frac{58.5\times2}{44.5} = 2.63$

The nearest whole no. of 2.63 = 3
$\therefore$ approximate at wt. of the element
$= 9 \times 3 = 27$

Ex.7 6.90 gm of a metal carbonate were dissolved in 60 ml of 2(N) HCl. The excess acid was neutralized by 20 ml of 1(N) NaOH. What is the equivalent wt. of metal ?
(A) 40 (B) 20 (C) 19 (D) 39

(Ans. D)

Sol. Equiv. of HCl taken $= 60 \times 2 \times 10^{-3}$
Equiv. of HCl present after the reaction
$= 20 \times 1 \times 10^{-3}$
$\therefore$ Equiv. of HCl utilized $= 100 \times 10^{-3}$
$\therefore 100 \times 10^{-3}$ equiv. of metal carbonate
= 6.90 gm
$\therefore$ 1 equiv. of metal carbonate

$= \frac{6.90}{10^{-1}} = 69$ gm

$\therefore$ equiv. wt. of metal = 69 – 30 = 39
[because equiv. wt. of carbonate = 30]

Ex.8 10 ml of $\left(\frac{N}{2}\right)$ HCl, 30 ml of $\left(\frac{N}{10}\right)$ HNO_3 and 75 ml of $\left(\frac{N}{5}\right)$ HNO_3 are mixed, the normality of H^+ in the resulting solution is-
(A) 0.2 (B) 0.1 (C) 0.5 (D) 0.25

(Ans. A)

Sol. The equiv. of H^+ in 10 ml of $\left(\frac{N}{2}\right)$ HCl $= \frac{10}{2} \times 10^{-3}$

The equiv. of H^+ in 30 ml of $\left(\frac{N}{10}\right)$ HNO_3 $= \frac{30}{10} \times 10^{-3}$

The equiv. of H^+ in 75 ml of $\left(\frac{N}{5}\right)$ HNO_3 $= \frac{75}{5} \times 10^{-3}$

Hence, total equiv. of $H^+ = (5 + 3 + 15) \times 10^{-3} = 23 \times 10^{-3}$

total volume of solution = 115 ml

Hence, normality of H^+ in the resulting

mixture $= \frac{23 \times 10^{-3} \times 10^3}{115}$ (N) $= \left(\frac{N}{5}\right) = 0.2$ (N)

Ex.9 500 ml of 0.2 (M) H_2SO_4 are mixed with 250 ml of 0.1 (M) $Ba(OH)_2$, the normality of resulting solution is -

(A) 0.2 (B) 0.1 (C) 0.5 (D) 0.25

(Ans. A)

Sol. 500 ml of 0.2 (M) H_2SO_4

$= 500 \times 0.2 \times 10^{-3}$ moles of H_2SO_4

$= 0.5 \times 0.2 \times 2$ equiv. of H_2SO_4

= 0.2 equiv. of H_2SO_4 250 ml of 0.1 (M) $Ba(OH)_2$

$= 250 \times 0.1 \times 10^{-3}$ moles of $Ba(OH)_2$

$= 250 \times 0.1 \times 10^{-3} \times 2$

= 0.05 equiv. of $Ba(OH)_2$

$\therefore$ Excess $H_2SO_4 = 0.2 - 0.05 = 0.15$ equiv.

Hence normality of H_2SO_4 in resulting solution $= \frac{0.15}{750} \times 1000 = 0.2$ (N)

Ex.10 What weight of $H_2C_2O_4 . 2H_2O$ (mol. wt. = 126) should be dissolved to prepare 250 ml of centinormal to be used as a reducing agent ?

(A) 0.63 gm (B) 0.1575 gm (C) 0.126 gm (D) 0.875 gm

(Ans. B)

Sol. Per mole of given acid $C_2O_4^{2-}$ present = 1 mole

$\therefore$ $C_2O_4^{2-} \longrightarrow CO_2 + 2e$

$\therefore$ x factor for $H_2C_2O_4 . 2H_2O$ as a reducing agent = 2

$\therefore$ equiv. wt. $= \frac{126}{2} = 63$

250 ml of centinormal solution

$= \frac{250}{100} \times 10^{-3}$ equiv.

wt. of $H_2C_2O_4 . 2H_2O$ required

$= \frac{250}{100} \times 10^{-3} \times 63$ gm $= 0.1575$ gm

Ex.11 Which of the following has the highest normality ? (consider each of the acid is 100% ionised.)

(A) 1 (M) H_2SO_4 (B) 1 (M) H_3PO_3 (C) 1 (M) H_3PO_4 (D) 1 (M) HNO_3

(Ans. C)

Sol. The normality of 1(M) H_2SO_4 = 2(N)
The normality of 1(M) H_3PO_3 = 2(N)
The normality of 1(M) H_3PO_4 = 3(N)
The normality of 1(M) HNO_3 = 1(N)

Ex.12 0.45 gm of an acid of mol. wt. 90 was neutralised by 20 ml of 0.5 (N) caustic potash (KOH). The basicity of acid is-

(A) 1 (B) 2 (C) 3 (D) 4

(Ans. B)

Sol. 20 ml of 0.5 (N) caustic potash
$= 20 \times 0.5 \times 10^{-3}$ equiv. of caustic potash
$\therefore 20 \times 0.5 \times 10^{-3}$ equiv. of acid = 0.45 gm

$\therefore$ 1 equiv. of acid = $\frac{0.45}{10\times10^{-3}}$ = 45 gm

$\therefore$ x for acid = $\frac{90}{45}$ = 2

Hence, basicity of acid = 2

Ex.13 The equivalent weight of a metal is double than that of oxygen. How many times is the weight of its oxide greater than the weight of metal ?

(A) 4 (B) 2 (C) 3 (D) 1.5

(Ans. D)

Sol. Equivalent mass of metal = $16 = \frac{x}{n}$

where x = atomic mass of metal
n = valency of metal
Molecular formula of metal oxide = M_2O_n

$$\frac{\text{Mass of metal oxide}}{\text{Mass of metal}} = \frac{2(16n)+16(n)}{2(16n)} = 1.5$$

Ex.14 On dissolving 2.0 g of metal in sulphuric acid, 4.51 g of the metal sulphate was formed. The specific heat of the metal is 0.057 cal g^{-1}. What is the valency of the metal and exact atomic mass?

Sol. Equivalent mass of SO_4^{2-} radical

$$= \frac{\text{Ionic mass}}{\text{Valency}} = \frac{96}{2} = 48$$

Mass of metal sulphate = 4.51g
Mass of metal = 2.0 g
Mass of sulphate radical = (4.51 – 2.0) = 2.51 g
2.51g of sulphate combine with 2.0 g of metal.
So, 48 g of sulphate will combine with

$= \frac{2}{2.51} \times 48 = 38.24$ g metal

Equivalent mass of metal = 38.24
According to Dulong and Petit's law,
Approximate atomic mass

$= \frac{6.4}{\text{Specific heat}} = \frac{6.4}{0.057} = 112.5$

Valency = $\frac{\text{Approximate atomic mass}}{\text{Equivalent mass}}$

$= \frac{112.5}{38.24} = 2.9 \approx 3$

Exact atomic mass = 38.24 × 3 = **114.72**

Ex.15 One gram of a chloride was found to contain 0.835 g of chlorine. Its vapour density is 85. Calculate its molecular formula :

Sol. Mass of metal chloride = 1g

Mass of chlorine = 0.835 g

Mass of metal = (1 – 0.835) = 0.165 g

Equivalent mass of metal = $\frac{0.165 \times 35.5}{0.835} = 7.01$

Valency of the metal = $\frac{2\,V.D.}{E + 35.5} = \frac{2 \times 85}{7.01 + 35.5} = 4$

Formula of the chloride = MCl_4

Ex.16 0.789 g of crystalline barium hydroxide is dissolved in water. For the neutralization of this solution. 20 mL of $\frac{N}{4}$ HNO_3 is required. How many molecules of water are present in one g mole of this base? (Ba = 137.4, O = 16, N = 14, H = 1)

Sol. Let the molecular formula be $Ba(OH)_2.xH_2O$ Mol. mass of $Ba(OH)_2.xH_2O$

= 137.4 + (2 × 16) + 2 × 1 + 18x = 171.4 + 18x

Eq. mass of $Ba(OH)_2.xH_2O = \frac{171.4 + 18x}{2}$ 20 mL $\frac{N}{4}$ $HNO_3 \equiv$ 20 mL $\frac{N}{4}$ $Ba(OH)_2.xH_2O$

Amount of $Ba(OH)_2.xH_2O = \frac{(171.4 + 18x)}{2 \times 4} \times \frac{20}{1000} = \frac{171.4 + 18x}{400}$ g

Amount of $Ba(OH)_2.xH_2O$ = 0.789 g

Hence, $\frac{171.4 + 18x}{400} = 0.789$

or 171.4 + 18x = 0.789 × 400 $x = \frac{144.2}{18} = 8.01 \approx$ **8**

Thus, 8 moles of water molecules are present in one mole of the base.

Ex.17 0.5 g mixture of $K_2Cr_2O_7$ and $KMnO_4$ was treated with excess of KI in acidic medium. Iodine liberated required 100 cm^3 of 0.15 N sodium thiosulphate solution for titration. Find the per cent amount of each in the mixture :

Sol. Let 'a' g of $K_2Cr_2O_7$ be present in the mixture.

Mass of $KMnO_4$ = (0.5 – a)g

Eq. mass of $K_2Cr_2O_7 = \frac{\text{Mol. mass}}{6} = \frac{294}{6} = 49.0$

Eq. mass of $KMnO_4 = \frac{\text{Mol. mass}}{5} = \frac{158}{5} = 31.6$

No. of equivalents of $K_2Cr_2O_7 = \frac{a}{49.0}$

No. of equivalents of $KMnO_4 = \frac{(0.5 - a)}{31.6}$

No. of equivalents of $Na_2S_2O_3$ in 100 cm^3 of 0.15 N solution = $\frac{100\times0.15}{1000}$ = 0.015

Equivalents of $K_2Cr_2O_7$ + Equivalents of $KMnO_4$
≡ Equivalents of iodine
≡ Equivalents of $Na_2S_2O_3$

$$\frac{a}{49.0}+\frac{(0.5-a)}{31.6}=0.015$$

17.4a = 1.274
a = 0.0732

% of $K_2Cr_2O_7 = \frac{0.0732\times100}{0.5}$ = 14.64
% of $KMnO_4$ = **85.36**

Ex.18 In an ore the only oxidisable material is Sn^{2+}. This ore is titrated with a dichromate solution containing 2.5 g $K_2Cr_2O_7$ in 0.50 litre. A 0.40 g of sample of the ore required 10.0 cm^3 of the titrant to reach equivalent point. Calculate the percentage of tin in ore. (K = 39.1, Cr = 52, Sn = 118.7)

Sol. Mol. mass of $K_2Cr_2O_7$ = 2 × 39.1 + 2 × 52 + 7 × 16
= 78.2 + 104.0 + 112.0
= 294.2

Eq. mass of $K_2Cr_2O_7 = \frac{294.2}{6}$ = 49.03

Normality of $K_2Cr_2O_7$ solution

$$=\frac{2.5}{49.03}\times\frac{1000}{500}=\frac{5}{49.03}\text{N}$$

10 mL $\frac{5}{49.03}$ N $K_2Cr_2O_7 \equiv$ 10 mL $\frac{5}{49.03}$ N stannous ion

Eq. mass of $Sn^{2+} = \frac{118.7}{2}$ = 59.35

Amount of Sn in the sample = $\frac{5}{49.03}\times\frac{59.35}{1000}\times10$ = 0.0605 g

Percentage of Sn in the ore = $\frac{0.0605}{0.40}\times100$ = 51

Ex.19 The percentage of an element M is 53 in its oxide of molecular formula M_2O_3. Its atomic mass is about
(A) 45 (B) 9 (C) 18 (D) 27

(Ans. D)

Sol. Equivalent mass of element

$$=\frac{\text{Mass of element}}{\text{Mass of oxygen}}\times8=\frac{53}{47}\times8\simeq9$$

Atomic mass = Equivalent mass × Valency
= 9 × 3 = 27 amu.

Ex.20 A solution containing 2.7×10^{-3} mol of A^{+n} ions requires 1.6×10^{-3} mole of MnO^{-}_4 for the oxidation of A^{+n} to AO^{-}_3 in acidic medium. What is the value of n –
(A) 1 (B) 2 (C) 3 (D) 4

(Ans. B)

Sol. The reaction are
$MnO^-_4 + 8H^+ + 5e^- \rightarrow Mn^{+2} + 4H_2O$
$A^{+n} + 3H_2O \rightarrow AO_3^- + 6H^+ + (5-n)\, e^-$
Amount of electrons involved in the given amount of MnO_4^- = $\frac{5}{3}$ x 1.6 x 10^{-3} mol.
Equating these two we get $5 \times 1.6 \times 10^{-3} = (5-n)\ 2.7 \times 10^{-3}$
$\therefore$ n = 2 (approx.)

Ex.21 One mole of As_2S_3 is oxidized by HNO_3 to H_3AsO_4 and H_2SO_4. HNO_3 is converted into NO. The moles of HNO_3 required are :
(A) 3 (B) 28 (C) 14 (D) 9.33

(Ans. D)

Sol. $(As^{3+})_2 \longrightarrow 2As^{5+} + 4e$

$(S^{2-})_3 \longrightarrow 3S^{6+} + 24e$

$As_2S_3 \longrightarrow 2As^{5+} + 3S^6 + 28e \times 3$

$3e + N^{5+} \longrightarrow N^{2+} \times 28$

3 mole of As_2S_3 are oxidized by 28 mole HNO_3.

(Ans. C)

Class Room Problems

1. A volume of 12.53 ml of 0.051 M SeO_2 reacts exactly with 25.5 ml of 0.1 M $CrSO_4$ which is oxidised to Cr^{3+}. To what oxidation state was the selenium converted by the reaction.

Sol. Zero

2. In basic solution CrO_4^{2-} ion oxidises $S_2O_3^{2-}$ ion to form $Cr(OH)_4^-$ and SO_4^{2-} ions respectively. How many ml of 0.154 Na_2CrO_4 solution are required just to react with 40 ml of 0.246 M $Na_2S_2O_3$ solution.

Sol. 170 ml

3. 25 ml of 0.17 M HSO_3^- in strongly acidic solution required the addition of 16.9 ml of 0.1 M MnO_4^- for its complete oxidation to SO_4^{2-}. In neutral solution it requires 28.6 ml. Assign oxidation no. of 'Mn' in each of the products.

Sol. 2,4

4. A given amount of Fe^{2+} is oxidised by x mol of MnO_4^- in acidic medium. Calculate mol of $Cr_2O_7^{2-}$ required same amount of Fe^{2+} in acidic medium

Sol. 5x/6 mole

5. Calculate mol of (a) MnO_4^- and (b) $Cr_2O_7^{2-}$ to oxidise 1 mol of FeC_2O_4 (ferrous oxalate) in acidic medium.

Sol. 3/5 and 1/2

6. A mixture of $Na_2C_2O_4$ and $KHC_2O_4.H_2C_2O_4$ required equal volume of 0.1 M $KMnO_4$ and 0.1 M NaOH separately. What is the molar ratio of $Na_2C_2O_4$ and $KHC_2O_4.H_2C_2O_4$ in the mixture?

Sol. 11/2

7. 5.5 gm of a mixture of $FeSO_4.7H_2O$ and $Fe_2(SO_4)_3.9H_2O$ requires 5.4 ml of 0.1 N $KMnO_4$ solution for complete oxidation. Calculate the no. of gm moles of hydrated ferric sulphate in the mixture?

Sol. 9.5×10^{-3} mole

8. 19.6 gm of ferrous ammonium sulphate [$FeSO_4(NH_4)_2SO_4.6H_2O$] were dissolved and made up to 500 ml with acidified water. 25 ml of this solution required 20 ml and 27.5 ml of the solution A and B of $KMnO_4$ respectively. How many ml of A must be added to 1 litre of B to make N/10 $KMnO_4$ solution.

Sol. 370

9. 0.5 gm of an oxalate was dissolved in water and the solution raised to 100 ml. 10 ml of this solution when titrated with N/20 $KMnO_4$ required 10 ml of $KMnO_4$. Calculate the % of oxalate ion in the sample.
(K = 39, Mn = 55)

Sol. 44%

10. Hydroxylamine reduced iron (+3) according to eq. $2NH_2OH + 4Fe^{+++} \rightarrow N_2O(g) + H_2O + 4Fe^{++} + 4H^+$. Iron (+2) thus produced is estimated by titration with a standard solution of permagnate. The reaction is $MnO_4^- + 5Fe^{++} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{+++} + 4H^2O$. A 10 ml solution of hydroxylamine solution was diluted to 1 litre 50 ml of this solution was boiled with an excess of iron (+3) solution. The resulting solution required 10 ml of 0.02 M $KMnO_4$ solution for complete oxidation or iron (+2). Calculate the weight of hydroxylamine in one litre of the original solution.

Sol. 39.6 g/ℓ

11. A 10 gm mixture of Cu_2S and CuS was treated with 200 ml of 0.75 M MnO_4^- in acid solution, producing SO_2, Cu^{2+} and Mn^{2+}. The SO_2 was boiled off and the excess of MnO_4^- was titrated with 175 ml of 01.0 M Fe^{2+} solution. Calculate the % CuS in the original solution.

Sol. 57.94 %

12. A solution of 0.2 gm of a compound containing Cu^{2+} and $C_2O_4^{2-}$ ions on titration with 0.02 M $KMnO_4$ in presence of H_2SO_4 consume 22.6 ml of the oxidant. The resultant solution is neutralized with Na_2CO_3, acidified with dilute acetic acid and treated with excess KI. The liberated I_2 required 11.3 ml of 0.05 M $Na_2S_2O_3$ solution for complete reduction. Find out the mole ratio of Cu^{++} and $C_2O_4^{2-}$ in the compound.

Sol. 1/2

13. 5 ml 8N HNO_3, 4.8 ml of 5N HCl, 1.4 gm of NaOH and a certain volume of 17 M H_2SO_4 are mixed together and made upto 2 litres. 50 ml of this solution exactly neutralized 32.9 ml of barium hydroxide solution containing 2.21 gm of $Ba(OH)_2$, $8H_2O$ in 100 ml of solution. Calculate (a) the volume H_2SO_4 used (b) The amount in grams of sulphate ion in the solution.

Sol.(a) 2.4 ml (b) 6.5 gm

14. A polyvalent metal weighing 0.1 gm and having at. wt. 51 reacted with dil. H_2SO_4 to give 43.9 ml of hydrogen at S.T.P. The solution containing the metal in this lower oxidation state, was found to require 58.8 ml of 0.1 N permagnate for complete oxidation. What are the valencies of the metal.

Sol. 2,5

15. A sample of ferrous sulphate and ferrous oxalate was dissolved in dil. H_2SO_4. The compete oxidation of reaction mixture require 40 ml of N/15 $KMnO_4$. After the oxidation the reaction mixture was reduced by zn and H_2SO_4. On again oxidation by same $KMnO_4$ 25 ml of $KMnO_4$ was required. Calculate the ratio of Fe atoms in ferrous sulphate and oxalate.

Sol. 7/3

16. A sample of $Fe_2(SO_4)_3$ and FeC_2O_4 was dissolved in dil H_2SO_4. The complete oxidation of reaction mixture req. 40 ml of N/16 $KMnO_4$. After the oxidation mixture was reduced by Zn and dil. H_2SO_4. On again oxidation by same $KMnO_4$, 60 ml were require. Calculate the ratio of millimoles of $Fe_2(SO_4)_3$ and FeC_2O_4 in mixture.

Sol. 7 : 6

17. A 6.0 gm sample contained Fe_3O_4, Fe_2O_3 and inert materials. It was treated with an excess of KI in acid, which reduced all iron to Fe^{2+}. The resulting solution was diluted to 50 ml, and a 10 ml sample of it was taken. The liberated iodine in the small sample was titrated with 5.5 ml of 1M $Na_2S_2O_3$ solution yielding $S_4O_6^{2-}$. The iodine from another 25 ml sample was extracted, after which the Fe^{2+} was titrated with 3.2 ml of 1.0 M MnO_4^- in H_2SO_4 solution. Calculate the percentage of Fe_3O_4 and Fe_2O_3, in the original mixture.

Sol. 34.8, 49.33

19. A 50.0 cm^3 portion of a mixture of H_2SO_4 and $H_2C_2O_4$ required 48.9 cm^3 of 0.15 M NaOH solution for titration. Another 50 cm^3 required 38.9 cm^3 of 0.10 N $KMnO_4$ solution for titration. Calculate the masses of H_2SO_4 and $H_2C_2O_4$ present per dm^3 of the solution.

Sol. 3.38 g, 3.501 g

20. A 5.0 cm^3 solution of H_2O_2 liberates 0.508g of iodine from an acidified KI solution. Calculate the strength of H_2O_2 solution in terms of volume strength at STP. **[JEE' 1995]**

Sol. 4.48%

21. A 3.00 g sample containing Fe_3O_4, Fe_2O_3 and an inert impure substance, is treated with excess of KI solution in presence of dilute H_2SO_4. The entire iron is converted into Fe^{2+} along with the liberation of iodine. The resulting solution is diluted to 100 ml. A 20 ml of the diluted solution require. 11.0 ml of 0.5 M $Na_2S_2O_3$ solution to reduce the iodine present. A 50 ml of the diluted solution, after complete extraction of the iodine requires 12.80 ml of 0.25 M $KMnO_4$ solution in dilute H_2SO_4 medium for the oxidation of Fe^{2+}. Calculate the percentages of Fe_2O_3 and Fe_3O_4 in the original sample. **[JEE'96, 5]**

Sol. Fe_2O_3 = 49.33 %, Fe_3O_4 = 34.8%

22. One litre of a mixture of O_2 and O_3 at NTP was allowed to react with an excess of acidified solution of KI. The iodine liberated required 40 ml of $\frac{M}{10}$ sodium thiosulphate solution for titration. What is the percent of ozone in the mixture? Ultraviolet radiation of wavelength 300 nm can decompose ozone. Assuming that one photon can decompose one ozone molecule, how many photons would have been required for the complete decomposition of ozone in the original mixutre ?**[JEE'97, 5]**

Sol. 6.57 % O_3 (By weight), 1.2×10^{21} photons

23. An aqueous solution containing 0.10 g KIO_3 (formula wt. = 214.0) was treated with an excess of KI solution. The solution was acidified with HCl. The liberated I_2 consumed 45.0 ml of thiosulphate solution to decolourise the blue starch - iodine complex. Calculate the molarity of the sodium thiosulphate solution. **[JEE' 1998]**

Sol. 0.0623 M

24. How many millilitre of 0.5 M H_2SO_4 are needed to dissolve 0.5 gm of copper II carbonate ? **[JEE' 1999]**

Sol. 8.097ml

25. Hydrogen peroxide solution (20 mL) reacts quantitatively with a solution of $KMnO_4$ (20 mL) acidified with dilute H_2SO_4. The same volume of the $KMnO_4$ solution is just decolorized by 10 mL of $MnSO_4$ in neutral medium simultaneously forming a dark brown precipitate of hydrated MnO_2. The brown precipitate is dissolved in 10 mL of 0.2 M sodium oxalate under boiling condition in the presence of dilute H_2SO_4. Write the balanced equations involved in the reactions and calculate the molarity of H_2O_2. **[JEE' 2001]**

Sol. 0.1M

EXERCISE – I OBJECTIVE PROBLEMS (JEE MAIN)

1. The equivalent weight of $MnSO_4$ is half its molecular weight when it is converted to :

(A) Mn_2O_3 (B) MnO_2

(C) MnO_4^- (D) MnO_4^{2-}

Sol.

2. Given the equation $S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$, $Mn^{2+} + 4H_2O \rightarrow MnO_4^- + 8H^+ + 5e^-$. How many moles of $S_2O_8^{2-}$ ions are require to oxiDes 1 mole of Mn^{2+}:

(A) 0.4 (B) 0.5

(C) 2.5 (D) 1.0

Sol.

3. A solution of 10 ml 0.1 M $FeSO_4$ was titrated with $KMnO_4$ solution in acidic medium. The amount of $KMnO_4$ used will be:

(A) 5 ml of 0.1 M (B) 10 ml of 0.1 M

(C) 10 ml of 0.5 M (D) 10 ml of 0.02 M

Sol.

4. NH_2OH reacts with ferric sulphate as follows : $2NH_2OH + 4\ Fe^{3+} \rightarrow N_2O + H_2O + 4\ Fe^{2+}\ 4H^+$. The eq. wt. of NH_2OH in this reaction is :

(A) (mol. wt.)/1 (B) (mol.wt.)/2

(C) (mol.wt.)/3 (D) (mol.wt.)/4

Sol.

5. 20 ml of 0.1 M solution of metal ion reaCteD with 20 ml of 0.1 M SO_2 solution. SO_2 reacted according to the equation. $SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^{+-} + 2e^-$. If the oxidation no. of metal ion was +3, the new oxidation number of the metal would be:

(A) 0 (B) +1

(C) +2 (D) None of these

Sol.

6. How many ml of 0.150 M Na_2CrO_4 will be required to oxidize 40 ml of 0.5 M $Na_2S_2O_3$.

$CrO_4^{2-} + S_2O_3^{2-} \rightarrow Cr(OH)_4^- + SO_4^{2-}$.

(A) 225 ml (B) 355 ml

(C) 455 ml (D) 555 ml

Sol.

7. Number of moles of electrons take up when 1 mole of NO_3^- ions is reduced to 1 mole of NH_2OH is:

(A) 2 (B) 4

(C) 5 (D) 6

Sol.

8. The number of moles of thiosulphate ($S_2O_3^{2-}$) that will required to react completely with one mole I_2 in alkaline medium (where it gets oxidised to SO_4^{2-}) is :

(A) 1/4 (B) 4

(C) 8 (D) 1/8

Sol.

9. The number of moles of oxalate $KHC_2O_4 . H_2C_2O_4 . 2H_2O$ oxidised by one mole of permanganate ion is:

(A) 3/4 (B) 1

(C) 5/4 (D) 6/4

Sol.

10. How many equivalents are there per mol of H_2S in its oxidation to SO_2 ?

(A) 2 (B) 4

(C) 6 (D) 8

Sol.

11. 3 mol of a mixture of $FeSO_4$ and $Fe_2(SO_4)_3$ required 100 mL of 2M $KMnO_4$ solution is acidic medium .

Hence mol fraction of $FeSO_4$ in the mixture is:

(A) 1/3 (B) 2/3

(C) 2/5 (D) 3/5

Sol.

12. In a reaction 4 moles of electron are transferred to one mole of HNO_3. When acted as an oxidant. The possible reduction product is :

(A) 1/2 mole of N_2 (B) 1/2 mole of N_2O

(C) 1 mole of NO_2 (D) 1 mole of NH_3

Sol.

13. One mole of N_2H_4 loses ten moles of electrons to from a new Compound y. Assuming that all the nitrogen appears in the new compound. What is the oxidation state of nitrogen in y. There is no change in the oxidation state of hydrogen:

(A) –1 (B) –3

(C) + 3 (D) +5

Sol.

14. 1 g equiv of a substance is the weight of that amount of a substance which is equivalent to :

(A) 0.25 mol of O_2 (B) 0.50 mol of O_2

(C) 1 mol of O_2 (D) 8 mol of O_2

Sol.

15. Which of the following changes requires reducing agent?

(A) $CrO_4^{2-} \rightarrow Cr_2O_7^{2-}$ (B) $BrO_3^- \rightarrow BrO^-$

(C) $H_2AO_3 \rightarrow HAsO_4^{2-}$ (D) $Al(OH)_3 \rightarrow Al(OH)_4^-$

Sol.

16. Which of the following is a disproportonation reaction?

(A) $CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2O + CO_2$

(B) $2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2+} + H_2O$

(C) $Cr_2O_4^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$

(D) $Cu_2O + 2H^+ \rightarrow Cu + Cu^{2+} + H_2O$

Sol.

17. If equal volumes of 1M $KMnO_4$ and 1M $K_2Cr_2O_7$ solutions are allowed to oxidise Fe^{2+} in acidic medium.

The amount of iron oxidised will Be :

(A) more by $KMnO_4$ solution

(B) more by $K_2Cr_2O_7$ solution

(C) equal in both the cases

(D) cannot be determined

Sol.

18. In the following reaction (unbalanced), equivalent wt. of As_2S_3 is related to molecular wt. M By:

$As_2S_3 + H^+ NO_3^- \rightarrow NO + H_2O + AsO_4^{3-} + SO_4^{2-}$

(A) M/2 (B) M/4

(C) M/28 (D) M/24

Sol.

19. Mass of KHC_2O_4 (potassium acid oxalate) required to reduce 100 mL of 0.02 M $KMnO_4$ in acidic medium (to Mn^{2+}) is x g, and to neutralise 100 mL of 0.05 M $Ca(OH)_2$ is y g then :

(A) x = y (B) 2x = y

(C) x = 2y (D) None is CorreCt

Sol.

20. 100 mL of 1 M $KMnO_4$ oxidised 100 mL of H_2O_2 in acidic medium (when MnO_4^- is reduced to Mn^{2+}) ; volume of same $KMnO_4$ required to oxidise 100 mL of H_2O_2 in basic medium (when MnO_4^- is reduced to MnO_2) will be:

(A) (100/3) mL (B) (500/3) mL

(C) (300/5) mL (D) 100 mL

Sol.

21. 1 mol of ferric oxalate is oxidised by x mol of MnO_4^- and also 1 mol of ferrous oxalate is oxidised By y mol of MnO_4^- in acidic medium. The ratio (x/y) is:

(A) 2 : 1 (B) 1 : 2

(C) 3 : 1 (D) 1 : 3

Sol.

22. 0.7 gm of $Na_2CO_3.xH_2O$ is dissolved in 100 ml, 20 ml of which required 19.8 ml of 0.1 N HCl. The value of x is:

(A) 4 (B) 3

(C) 2 (D) 1

Sol.

23. A metal is burnt in oxygen and all the products of combustion are weighed. It is found that the wt. of the metal seems to have increased by 24%. The equivalent wt. of the above metal.

(A) 25 (B) 24

(C) 33.34 (D) 76

Sol.

24. When one gm mole of $KMnO_4$ reacts with HCl, the volume of chlorine liberated at NTP will be:

(A) 11.2 litre (B) 22.4 litre

(C) 44.8 litre (D) 56.0 litre

Sol.

25. 10.78 g of H_3PO_4 in 550 mL solution is 0.40 N. Thus this acid:

(A) has been neutralised to HPO_4^{2-}

(B) has been neutralised to PO_4^{3-}

(C) has been reduced to HPO_3^{2-}

(D) has been neutralised to $H_2PO_4^-$

Sol.

26. When 0.75 gm of a substance was kjeldalised, it produced NH_3. Which neutralizes 30 ml of 0.25 N sulphuric acid. The percentage of nitrogen in the organic compound is :

(A) 14 (B) 11

(C) 1 (D) None

Sol.

27. 15 mol of $KMnO_4$ are treated with excess $H_2C_2O_4$ in H_2SO_4 medium. How many moles of CO_2 will be formed and how many moles of $H_2C_2O_4$ will be consumed?

(A) 75, 37, 5. (B) 3, 15

(C) 3, 6 (D) 75, 150

Sol.

28. An equimolar mixture of $NaHC_2O_4$ and $H_2C_2O_4$ consumes 20 ml 0.3 M NaOH solution for complete neutralization. The same mixture requires V ml. 0.05 M $KMnO_4$ solution in acidic medium for oxidation.

The value of V is :

(A) 160 ml (B) 32 ml

(C) 24 ml (D) None of these

Sol.

29. Oxidation number of Fe in Fe_3O_4 is fractional because-

(A) It is a mixed [Fe(+2) – Fe(+4)] oxide

(B) It is a non-stoichiometric compound

(C) It is a mixed [Fe(+2) – Fe(+3)] oxide

(D) None of the above

Sol.

30. The oxidation state of Oxygen atom in potassium superoxide is-

(A) Zero (B) $-\frac{1}{2}$

(C) – 1 (D) – 2

Sol.

31. The oxidation state of tungsten in $Na_2W_4O_{13}.10H_2O$ is –

(A) + 7 (B) + 6

(C) + 4 (D) + 4.5

Sol.

32. Amongst the following identify the species with an atom in +6 oxidation state –

(A) MnO_4^- (B) $Cr(CN)_6^{3-}$

(C) NiF_6^{2-} (D) CrO_2Cl_2

Sol.

33. In $[Cr(O_2)(NH_3)_4(H_2O)]Cl_2$ oxidation number of Cr is + 3, then O_2 will be in the form :

(A) dioxide (B) peroxide

(C) superoxide (D) oxide

Sol.

34. An example of redox process is –

(A) $CuSO_4 + Fe \rightarrow FeSO_4 + Cu$

(B) $Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O$

(C) $CaO + 2HCl \rightarrow CaCl_2 + H_2O$

(D) $CaCO_3 \xrightarrow{heat} CaO + CO_2$

Sol.

35. In the reduction of dichromate by Fe(II), the number of electrons involved per chromium atom is –

(A) 3 (B) 1

(C) 2 (D) 4

Sol.

36. Consider the following statement in the reaction
$KIO_3 + 5KI + 6HCl = 3I_2 + 6KCl + 3H_2O$
(a) KI is oxidised to I_2
(b) KIO_3 is oxidised to I_2
(c) KIO_3 is reduced to I_2
(d) Oxidation number of I increases from (–1) in KI to zero in I_2 of these statements
(A) a, c and d are correct
(B) a, b and d are correct
(C) b and d are correct
(D) a alone is correct

Sol.

37. Match list – I (compounds) with list – II (Oxidation state of nitrogen) and select the correct answer using the codes given below the lists –

List – I	List – II
(A) NaN_3	(a) +5
(B) N_2H_4	(b) +2
(C) NO	(c) –1/3
(D) N_2O_5	(d) –2

Codes :–

	A	B	C	D
(A)	c	d	b	a
(B)	d	c	b	a
(C)	c	d	a	b
(D)	d	c	a	b

Sol.

38. In the reaction,
$3Br_2 + 6NaOH \rightarrow NaBrO_3 + 5NaBr + 3H_2O$ which element loses as well as gains electrons –
(A) Na (B) Br
(C) O (D) H

Sol.

39. Oxidation number of S in $H_2S_2O_7$ is –
(A) +4 (B) –6
(C) –5 (D) +6

Sol.

40. Oxidation number of S in H_2SO_5 is 6. This is observed, because –
(A) There are five oxygen atoms in the molecule
(B) The hydrogen atom is directly linked with non-metal
(C) There is peroxide linkage in the molecule
(D) The sulphur atom shows co-ordinate linkage

Sol.

41. The oxidation number of S in $Na_2S_4O_6$ is -
(A) + 2.5
(B) + 2 and + 3 (two S have + 2 and other two have + 3)
(C) + 2 and + 3 (three S have + 2 and one S has + 3)
(D) + 5 and 0 (two S have + 5 and the other two have 0)

Sol.

42. The oxidation state of molybdenum in its oxocomplex species $[Mo_2O_4(C_2H_4)_2(H_2O)_2]^{2-}$ is

(A) +2 (B) +3

(C) +4 (D) +5

Sol.

43. Which element will have the maximum oxidation number in $K_2Cr_2O_7$ and $KMnO_4$ –

(A) Mn (B) Cr

(C) O (D) K

Sol.

44. Select the pair of oxidation processes,

(a) $2Cu^{2+} \rightarrow Cu_2^{2+}$

(b) $MnO_4^- \rightarrow Mn^{2+}$

(c) $[Fe(CN)_6]^{-4} \rightarrow [Fe(CN)_6]^{-3}$

(d) $2I^- \rightarrow I_2$

(A) a, b (B) c, d

(C) a, d (D) b, c

Sol.

45. Carbon is in the lowest oxidation state in –

(A) CH_4 (B) CCl_4

(C) CF_4 (D) CO_2

Sol.

46. $AB_4^- + C^{+2} \rightarrow C^{+3} + A^{+2}$

If the O.N. of B is –2. Choose the true statement for the above change –

(A) O.N. of A decreases by –5

(B) O.N. of C decreases by +1

(C) O.N. of A decreases by + 5 and that of C increases by +1

(D) O.N. of A decreases by +5 and that of C decreases by +1

Sol.

47. Oxygen shows oxidation state of –1 in the compound –

(A) NO_2 (B) MnO_2

(C) PbO_2 (D) Na_2O_2

Sol.

48. The oxidation number of Pt in $[Pt(C_2H_4)Cl_3]^-$ is –

(A) +1 (B) +2

(C) +3 (D) +4

Sol.

49. Which of the following reactions does not involve either oxidation or reduction –

(A) $VO^{2+} \rightarrow V_2O_3$ (B) $Na \rightarrow Na^+$

(C) $Zn^{+2} \rightarrow Zn$ (D) $CrO_4^{-2} \rightarrow Cr_2O_7^{-2}$

Sol.

50. Which one is correctly matched:

Substance	O.N. of S
(A) H_2S	+2
(B) H_2SO_5	+4
(C) H_2SO_4	+4
(D) $Na_2S_4O_6$	+2.5

Sol.

EXERCISE – II OBJECTIVE PROBLEMS (JEE ADVANCED)

Multiple choice Question.

1. In the titration of $K_2Cr_2O_7$ and ferrous sulphate, following data is obtained: V_1 ml of 1.0 M_1 $K_2Cr_2O_7$ requires V_2 ml of 1.0 M_2 $FeSO_4$. Which of the following relations is/are true for the above titration ?

(A) $6\ M_1V_1 = M_2V_2$ (B) $M_1V_1 = 6\ M_2V_2$

(C) $N_1V_1 = N_2V_2$ (D) $M_1V_1 = M_2V_2$

Sol.

2. $Cr_2O_7^{2-}$ is reduced to Cr^{3+} by Fe^{2+}. Identify the correct statement from the following :

(A) 6 moles of Fe^{2+} are oxidised to Fe^{3+} ions.

(B) The solution becomes yellow

(C) The solution becomes green

(D) 3 moles of Fe^{2+} get oxidised to Fe^{3+}

Sol.

3. 15 g of $KMnO_4$ in acidic medium equal to

(A) 0.095 moles

(B) 0.477 g equivalents

(C) 9.54 L of 0.05 N $KMnO_4$

(D) 10 ml of 0.05 M $KMnO_4$

Sol.

4. Which of the following statements are correct ?

(A) One mole of Cl_2 means 8 equivalents of chlorine when $Cl_2 \longrightarrow Cl^- + ClO_4^-$

(B) One mole of Cl_2 means 6 equivalents of chlorine when $Cl_2 \longrightarrow Cl^- + ClO_4^-$

(C) When one mole of As_2S_3 is oxidised to As_2O_5 + SO_2 then it mean 22 equivalents of As_2S_3 are oxidised.

(D) The equivalent weight of As_2S_3 is always = mol. wt./22.

Sol.

5. 27 g of Al will react completely with

(A) 24 g of O_2 (B) 0.75 mole of O_2

(C) 16.8 L of O_2 at STP (D) 1 mole of O_2

Sol.

6. 10.78 g of H_3PO_4 in 550 ml solution is 0.40 N. Thus this acid

(A) has been neutralized to HPO_4^{2-}

(B) has been neutralized to PO_4^{3-}

(C) has been reduced to HPO_3^{2-}

(D) has been neutralized to $H_2PO_4^-$

Sol.

7. Which of the following contains equal number of atoms ?

(A) 11.2 ml of N_2 and 0.015 g of nitric oxide

(B) 22.4 L of nitrous oxide and 22.4 L of CO_2

(C) 1 mole of HCl and 0.5 mole of H_2S

(D) 1 mole of H_2O_2 and 1 mole of H_2SO_4

Sol.

8. When 100 ml of 0.1 M KNO_3, 400 ml of 0.2 M HCl and 500 ml of 0.3 M H_2SO_4 are mixed. Then in the resulting solution

(A) The molarity of K^+ = 0.01 M

(B) The molarity of SO_4^{2-} = 0.15 M

(C) The molarity of H^+ = 0.38 M

(D) The molarity of NO_3^- = 0.08 M and Cl^- = 0.01 M

Sol.

9. A 110 % sample of oleum contains
(A) 44.4% of SO_3
(B) 55.6% of sulphuric acid
(C) 55.6% of SO_3
(D) 44.4% of sulphuric acid

Sol.

10. A mixture of 1 mole each of $FeSO_4$ and FeC_2O_4 are taken then :
(A) n_{moles} of $KMnO_4$ required to oxidise Fe^{2+} to Fe^{3+} in acidic medium is 0.4
(B) n_{moles} of $KMnO_4$ required to oxidise SO_4^{2-} is 6/5
(C) n_{moles} of $KMnO_4$ required to oxidise oxalate ion is 0.4
(D) The total number of moles of $KMnO_4$ required to completely oxidise the mixture is 0.8

Sol.

11. 100 ml of 0.06 M $Ca(NO_3)_2$ is added to 50 ml of 0.06 M $Na_2C_2O_4$. After the reaction is complete
(A) 0.003 moles of calcium oxalate will get precipitated
(B) 0.003 M of excess of Ca^{2+} will remain in excess
(C) $Na_2C_2O_4$ is limiting reagent.
(D) $Ca(NO_3)_2$ is excess reagent.

Sol.

12. To 25 ml of H_2O_2 solution, excess of acidified solution of KI was added. The iodine liberated required 20 ml of 0.1 N $Na_2S_2O_3$ solution. Calculate the % of H_2O_2 solution.
(A) 0.0136 % (B) 0.136 %
(C) 0.0068 % (D) 0.068 %

Sol.

13. 10 g mixture of KI and $NaClO_3$ treated with 200 cc HCl gives a gas which absorbes in 40 ml of $\frac{N}{10}$ sodium thiosulphate solution. Then the correct statement is/are
(A) equivalent weight of iodine in the reaction is M/2
(B) percentage of KI in the mixture is 66.4%
(C) sodium thiosulphate converted into $Na_2S_4O_6$.
(D) percentage of $NaClO_3$ is 66.4%

Sol.

14. $H_2C_2O_4$ and $NaHC_2O_4$ behave as acids as well as reducing agents. Which is/are correct statement(s) ?
(A) Equivalent wt. of $H_2C_2O_4$ and $NaHC_2O_4$ are equal to their molecular weights when behaving as reducing agent
(B) 100 ml of 1 N solution of each is neutralised by equal volumes of 1 M $Ca(OH)_2$
(C) 100 ml of 1 N solution of each is neutralised by equal volumes of 1 N $Ca(OH)_2$
(D) 100 ml of 1 M solution of each is oxidised by equal volumes of 1 M $KMnO_4$

Sol.

15. 100 ml of 0.15 N H_2O_2 is completely oxidized by
(A) 150 ml of 0.1 N $KMnO_4$ solution
(B) 2.5×10^{-3} moles of $K_2Cr_2O_7$ in acidic medium
(C) 15×10^{-3} moles of $KMnO_4$ in basic medium
(D) 15 moles of O_3 in acidic medium

Sol.

Question No. 16 to 19 (4 questions)

30cc of a solution containing 9.15 gm of salt $K_xH_Y(C_2O_4)_z.nH_2O$ per litre required 27cc of 0.12 N NaOH for neutralization. The same quantity of solution was also found to require 36cc of 0.12 N $KMnO_4$ solution for complete oxidation.

16. What is the value of X
(A) 1 (B) 2
(C) 3 (D) 4

Sol.

17. What is the value of Y
(A) 4 (B) 3
(C) 2 (D) 1

Sol.

18. What is the value of Z
(A) 4 (B) 1
(C) 2 (D) 3

Sol.

19. What is the value of n
(A) 4 (B) 3
(C) 1 (D) 2

Sol.

Question No. 20 to 22 (3 questions)

A steel sample is to be analysed for Cr and Mn simultaneously. By suitable treatment Cr is oxidized as $Cr_2O_7^{2-}$ and the Mn to MnO_4^-.

$Cr \rightarrow Cr_2O_7^{2-}$

$Mn \rightarrow MnO_4^-$

A 10 gm sample of steel is used to produce 250.0 mL of a solution containing $Cr_2O_7^{2-}$ and MnO_4^-. A 10 mL portion of this solution is added to a $BaCl_2$ solution and by proper adjustment of the acidity, the chromium is completely precipitated as $BaCrO_4$; 0.0549 g is obtained.

$$Cr_2O_7^{2-} \xrightarrow{H^{\oplus}} BaCrO_4$$

A second 10 mL portion of this solution requires exactly 15.95 mL of 0.0750 M standard Fe^{2+} solution for its titration (in acid solution)

20. % of chromium in the steel sample
(A) 1.496 (B) 2.82
(C) 1.96 (D) 5

Sol.

21. Equivalent of Fe^{2+} required for reduction of MnO_4^- is
(A) 5.44×10^{-4} (B) 0.544×10^{-2}
(C) 1.196×10^{-3} (D) 11.96×10^{-4}

Sol.

22. Amount of $BaCl_2$ required for conversion of $Cr_2O_7^{2-}$ to $BaCrO_4$ in steel sample
(A) 0.045 (B) 0.0549
(C) 1.125 (D) 2.82

Sol.

Question No. 23 to 25 (3 questions)

25 ml from a stock solution containing $NaHCO_3$ and Na_2CO_3 was diluted to 250 ml with CO_2 free distilled water. 25 ml of the diluted solution when titrated with 0.12 M HCl required 8 ml., when phenolphthalein was used as an indicator.

$$Na_2CO_3 + HCl \xrightarrow{HPh} NaHCO_3$$

When 20 ml of diluted solution was titrated with same acid it required 18 ml when methlyorange was used as an indicator.

$$Na_2CO_3 + 2HCl \xrightarrow{MeOH} 2NaCl + H_2O + CO_2$$

$$NaHCO_3 + HCl \xrightarrow{MeOH} NaCl + H_2O + CO_2$$

23. Concentration of $NaHCO_3$ in gm/lit.

(A) 0.312 (B) 2.62

(C) 3.12 (D) 26.208

Sol.

24. Amount of NaOH that should be added to convert all bicarbonate into carbonate in 100 ml stock solution

(A) 1.248 gm (B) 0.312 gm

(C) 3.12×10^{-2} gm (D) 7.8×10^{-3} gm

Sol.

25. Millimoles of $NaHCO_3$ present in stock solution

(A) 0.624 (B) 2.16

(C) 1.536 (D) 7.8

Sol.

Question No. 26 to 28 (3 questions)

1.16 g $CH_3(CH_2)_n$ COOH was burnt in excess air and the resultant gases (CO_2 and H_2O) were passed through excess NaOH solution. The resulting solution was divided in two equal parts. One part requires 50 mL of 1 N HCl for neutralization using phenolphthalein as indicator. Another part required 80 mL of 1 N HCl for neutralization using methyl orange as indicator.

26. Produced mole of the CO_2

(A) 0.1 (B) 0.01

(C) 0.06 (D) None of these

Sol.

27. What is the value of n

(A) 4 (B) 3

(C) 2 (D) 1

Sol.

28. Amount of excess NaOH solution taken initially.

(A) 3.2 gm (B) 6.4 gm

(C) 1.2 gm (D) None of these

Sol.

29. The oxidation number of phosphorus in $Ba(H_2PO_2)_2$ is - **[IIT-1990]**

(A) +3 (B) +2

(C) +1 (D) –1

Sol.

30. The compound which could act both as oxidising as well as reducing agent is -
[IIT-Screening 1991]

(A) SO_2 (B) $KMnO_4$

(C) Al_2O_3 (D) CrO_3

Sol.

31. The number of electrons to balance the following equation, the value of x is -
[IIT-Screening 1991]

$NO_3^- + 4H^+ + xe^- \rightarrow 2H_2O + NO$ is -

(A) 5 (B) 4

(C) 3 (D) 2

Sol.

32. The oxidation state of molybdenum in its oxo complex species $[Mo_2O_4(C_2H_4)_2\ (H_2O_2)]^{2-}$
[IIT-Screening 1991]

(A) 2 (B) 3

(C) 4 (D) 5

Sol.

33. The oxidation states of the most electronegative element in the products of the reaction, BaO_2 with dilute H_2SO_4 are - **[IIT- 1991]**

(A) 0 and –1 (B) –1 and –2

(C) –2 and 0 (D) –2 and +1

Sol.

34. For the readox reaction,

$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{+2} + CO_2 + H_2O$

the correct coefficients of the reactants for the balanced reaction are– **[IIT- 1992]**

	MnO_4^-	$C_2O_4^{2-}$	H^+
(A)	2	5	16
(B)	16	5	2
(C)	5	16	2
(D)	2	16	5

Sol.

35. What mass of N_2H_4 can be oxidised to N_2 by 24 gm of K_2CrO_4 which is reduced to $[Cr(OH)_4]^-$.

Sol.

36. The ion A^{n+} is oxidised to AO_3^- by MnO_4^- changing to Mn^{2+} in acid medium. Given that 2.68×10^{-3} mole of A^{n+} required 1.61×10^{-3} mole of MnO_4^-. What is the value of n.

Sol.

37. 2.180 gram of a sample contains a mixture of XO and X_2O_3 which are completely oxidised to XO_4^- by 0.015 mole of $K_2Cr_2O_7$. Calculate the atomic weight of X, if 0.0187 mole XO_4^- is formed.

Sol. 100

38. The number of moles of $KMnO_4$ that will be needed to react completely with one mole of ferrous oxalate in acid solution is **[JEE 1996]**

(A) 3/5 (B) 2/5

(C) 4/5 (D) 1

Sol.

39. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphite ions in acidic solution is **[JEE 1997]**

(A) 2/5 (B) 3/5

(C) 4/5 (D) 1

Sol.

Each of the questions given below consists of Statement – I and Statement – II. Use the following Key to choose the appropriate answer.

(A) If both Statement-I and Statement-II are true, and Statement-II is the correct explanation of Statement–I.

(B) If both Statement-I and Statement-II are true but Statement-II is not the correct explanation of Statement–I.

(C) If Statement-I is true but Statement-II is false.

(D) If Statement-I is false but Statement-II is true.

40. **Statement I:** $NaOH+H_3PO_4 \rightarrow NaH_2PO_4+H_2O$ in given reaction equivalent weight of H_3PO_4 is $\frac{M}{3}$.

Statement II : H_3PO_4 is tribasic acid.

Sol.

41. **Statement I :** In CuO equivalent weight of Cu is 63.5 & in Cu_2O equivalent weight of Cu is 31.8.

Statement II : Equivalent weight of any metal is the gm quantity of metal which is combined with 8 gm of oxygen in the formation of metal oxide.

Sol.

42. **Statement I :** In Pb_3O_4 all Pb has + $\frac{8}{3}$ oxidation number.

Statement II : Pb_3O_4 is mixed oxide of PbO & PbO_2

Sol.

43. **Statement I :** In estimation of $FeSO_4$ $KMnO_4$ along with HCl can be used as oxidising agent.

Statement II : In acidic medium $KMnO_4$ is more powerful oxidant compared to neutral/ basic medium.

Sol.

44.

Column - I	**Column- II**
(A) $Cr_2O_7^{-2} \rightarrow Cr^{+3}$	(P) $\frac{M}{7}$
(B) $Fe(NO_3)_3 \rightarrow Fe(NO_2)_2$	(Q) $\frac{M}{6}$
(C) $H_2O_2 \rightarrow O_2$	(R) M
(D) $PH_3 + H^+ \rightarrow PH_4^+$	(S) $\frac{M}{2}$

Sol.

Column Match

45.

Column I	**Column II**
(1) Increase in oxidation number	(a) Loss of electrons
(2) Decrease in oxidation number	(b) Redox reaction
(3) Oxidising agent	(c) Fractional oxidation number
(4) Reducing agent	(d) Zero oxidation number
(5) $2Cu^+ \rightarrow Cu^{2+} + Cu$	(e) Simple neutralisation reaction
(6) $MnO_2+4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$	(f) Gain of electrons
(7) $\underline{Mn}_3O_4$	(g) Disproportionation
(8) $\underline{C}H_2Cl_2$	(h) Oxidation
(9) $NaOH+HCl \rightarrow NaCl + H_2O$	(i) Reduction

Sol.

46. The normality of 0.3 M phosphorus acid (H_3PO_3) is

(A) 0.1 (B) 0.9

(C) 0.3 (D) 0.6 **[JEE 1999]**

Sol.

47. One mole of calcium phosphide on reaction with excess of water gives **[JEE 1999]**
(A) one mole of phosphine
(B) Two moles of phsophoric acid
(C) Two moles of phosphine
(D) One mole of phosphorus pentoxide

Sol.

48. An aqueous solution of 6.3 gm of oxalic acid dihydrate is made upto 250 ml. The volume of 0.1 N NaOH required to completely neutralize 10 ml of this solution is **[JEE 2001]**
(A) 40 ml (B) 20 ml
(C) 10 ml (D) 4 ml

Sol.

49. In the standarization of $Na_2S_2O_3$ using $K_2Cr_2O_7$ by iodometry the equivalent mass of $K_2Cr_2O_7$ is **[JEE 2001]**
(A) $\frac{\text{M.Mass}}{2}$ (B) $\frac{\text{M.Mass}}{6}$
(C) $\frac{\text{M.Mass}}{3}$ (D) Same as M. Mass.

Sol.

50. How many litres of a 0.5 N solution of an oxidising agent are reduced by 2 litres of a 2.0 N solution of a reducing agent ?
(A) 8 (B) 4
(C) 6 (D) 7 litres

Sol.

EXERCISE – III SUBJECTIVE PROBLEMS (JEE ADVANCED)

Balancing of reactions

1. Complete and balance the following equations

(a) $KMnO_4 + H_2SO_4 + H_2O_2 \rightarrow$

$K_2SO_4 + MnSO_4 + H_2O$ + ...

(b) $Cu^{2+} + I^- \rightarrow Cu^+ + I_2$

Sol.

2. Balance the following in basic medium

(i) $CrI_3 + H_2O_2 + OH^- \rightarrow CrO_4^{2-} + IO_4^- + H_2O$

(ii) $KOH + K_4Fe(CN)_6 + Ce(NO_3)_4 \rightarrow$

$Fe(OH)_3 + Ce(OH)_3 + K_2CO_3 + KNO_3 + H_2O$

Sol.

3. Balance the following equations using desired medium:

(a) $SbCl_3 + KIO_3 + HCl \rightarrow SbCl_5 + ICl + H_2O + KCl$

(b) $FeC_2O_4 + KMnO_4 + H_2SO_4 \rightarrow$

$Fe_2(SO_4)_3 + CO_2 + MnSO_4 + K_2SO_4 + H_2O$

Sol.

4. Balance the following equations using desired medium:

$FeCr_2O_4 + K_2CO_3 + KClO_3 \rightarrow$

$Fe_2O_3 + K_2CrO_4 + KCl + CO_2$

Sol.

5. Balance the following equations using desired medium:

$Pb(N_3)_2 + Co(MnO_4)_3 \rightarrow$

$CoO + MnO_2 + Pb_3O_4 + NO$

Sol.

6. Balance the following equations in acidic medium

$KClO_3 + H_2SO_4 \rightarrow KHSO_4 + HClO_4 + ClO_2 + H_2O$

Sol.

7. Balance the following equations in acidic medium

$Br^- + BrO_3^- + H^+ \rightarrow Br_2 + H_2O$

Sol.

8. Balance the following equations in acidic medium

$H_2S + Cr_2O_7^{2-} + H^+ \rightarrow Cr_2O_3 + S_8 + H_2O$

Sol.

9. Balance the following equations in acidic medium

$H_2S + Cr_2O_7^{2-} + H^+ \rightarrow Cr_2O_3 + S_8 + H_2O$

Sol.

10. Balance the following equations in acidic medium

$Cu_2O + H^+ + NO_3^- \rightarrow Cu^{2+} + NO + H_2O$

Sol.

11. Balance the following equations in acidic medium

$[Fe(CN)_6]^{4-} + MnO_4^- \rightarrow$

$Fe^{3+} + CO_2 + NO_3^- + Mn^{2+}$

Sol.

12. Balance following equations in proper medium
(a) $C_2H_5OH + MnO_4^- \rightarrow C_2H_3O^- + MnO_2(s) + H_2O$

Sol.

13. Balance following equations in proper medium
$Cr_2O_7^{2-} + C_2H_4O + H^+ \rightarrow C_2H_4O_2 + Cr^{3+}$

Sol.

14. Balance following equations in proper medium
$P + OH^- + H_2O \rightarrow H_2PO_4^- + PH_3$

Sol.

15. Balance following equations in proper medium
$S + OH^- \rightarrow S^{2-} + S_2O_3^{2-}$

Sol.

16. Balance following equations in proper medium
$Na_2S_2O_3 + KMnO_4 + H_2O \rightarrow$
$Na_2S_4O_6 + MnO_2 + KOH + NaOH$

Sol.

17. Balance following equations in proper medium
$FeC_2O_4 + KMnO_4 + H_2SO_4 \rightarrow$
$Fe_2(SO_4)_3 + CO_2 + MnSO_4 + K_2SO_4 + H_2O$

Sol.

18. Balance following equations in proper medium
$C_2H_5OH + I_2 + OH^- \rightarrow CHI_3 + HCOO^- + H_2O + I^-$

Sol.

Acid Base Titration

19. A solution containing 4.2 g of KOH and $Ca(OH)_2$ is neutralized by an acid. It consumes 0.1 equivalent of acid, calculate the percentage composition of the sample.

Sol.

20. How many ml of 0.1 N HCl are required to react completely with 1 g mixture of Na_2CO_3 and $NaHCO_3$ containing equimolar amounts of two ?

Sol.

21. 0.5 g of fuming H_2SO_4 (oleum) is diluted with water. The solution requires 26.7 ml of 0.4 N NaOH for complete neutralization. Find the % of free SO_3 in the sample of oleum.

Sol.

22. H_3PO_4 is a tri basic acid and one of its salt is NaH_2PO_4. What volume of 1 M NaOH solution should be added to 12 g of NaH_2PO_4 to convert it into Na_3PO_4 ?

Sol.

Double titration

23. A solution contains Na_2CO_3 and $NaHCO_3$. 20 ml of this solution required 4 ml of 1 N HCl for titration with Ph indicator. The titration was repeated with the same volume of the solution but with MeOH. 10.5 ml of 1 N HCl was required this time. Calculate the amount of Na_2CO_3 & $NaHCO_3$.

Sol.

24. A solution contains a mixture of Na_2CO_3 and NaOH. Using Ph as indicator 25 ml of mix required 19.5 ml of 1 N HCl for the end point. With MeOH, 25 ml of the solution required 25 ml of the same HCl for the end point. Calculate gms/L of each substance in the mixture.

Sol.

25. 200 ml of a solution of mixture of NaOH and Na_2CO_3 was first titrated with $\frac{N}{10}$ HCl with indicator Ph. 17.5 ml of HCl was required for end point. After this MeOH was added and 2.5 ml of same HCl was again required for next end point. Find out amounts of NaOH and Na_2CO_3 in the mixture.

Sol.

Redox Titration

26. It requires 40.05 ml of 1 M Ce^{4+} to titrate 20 ml of 1 M Sn^{2+} to Sn^{4+}. What is the oxidation state of the cerium in the product.

Sol.

27. A volume of 12.53 ml of 0.05093 M SeO_2 reacted with exactly 25.52 ml of 0.1 M $CrSO_4$. In the reaction, Cr^{2+} was oxidized to Cr^{3+}. To what oxidation state was selenium converted by the reaction.

Sol.

28. Potassium acid oxalate $K_2C_2O_4.3H_2C_2O_4.4H_2O$ can be oxidized by MnO_4^- in acid medium. Calculate the volume of 0.1 M $KMnO_4$ reacting in acid solution with one gram of the acid oxalate.

Sol.

29. A 1 g sample of H_2O_2 solution containing x% H_2O_2 by mass requires x cm^3 of a $KMnO_4$ solution for complete oxidation under acidic conditions. Calculate the normality of $KMnO_4$ solution.

Sol.

30. Metallic tin in the presence of HCl is oxidized by $K_2Cr_2O_7$ to stannic chloride, $SnCl_4$. What volume of deci-normal dichromate solution would be reduced by 1 g of tin.

Sol.

31. 5g sample of brass was dissolved in one litre dil. H_2SO_4. 20 ml of this solution were mixed with KI, liberating I_2 and Cu^+ and the I_2 required 20 ml of 0.0327 N hypo solution for complete titration. Calculate the percentage of Cu in the alloy.

Sol.

32. A 1.0 g sample of Fe_2O_3 solid of 55.2 % purity is dissolved in acid and reduced by heating the solution with zinc dust. The resultant solution is cooled and made upto 100.0 mL. An aliquot of 25.0 mL of this solution requires 17.0 mL of 0.0167 M solution of an oxidant for titration. Calculate the number of moles of electrons taken up by the oxidant in the reaction of the above titration.

Sol.

33. 0.84 g iron ore containing x percent of iron was taken in a solution containing all the iron in ferrous condition. The solution required x ml of a dichromatic solution for oxidizing the iron content to ferric state. Calculate the strength of dichromatic solution.

Sol.

34. 5 g of pyrolusite (impure MnO_2) were heated with conc. HCl and Cl_2 evolved was passed through excess of KI solution. The iodine liberated required 40 mL of $\frac{N}{10}$ hypo solution. Find the % of MnO_2 in the pyrolusite.

Sol.

Back Titration

35. 50 gm of a sample of $Ca(OH)_2$ is dissolved in 50 ml of 0.5 N HCl solution. The excess of HCl was titrated with 0.3N NaOH. The volume of NaOH used was 20cc. Calculate % purity of $Ca(OH)_2$

Sol.

36. One gm of impure sodium carbonate is dissolved in water and the solution is made up to 250ml. To 50ml of this solution, 50ml of 0.1N – HCl is added and the mixture after shaking well required 10ml of 0.16N NaOH solution for complete titration. Calculate the % purity of the sample.

Sol.

37. What amount of substance containing 60% NaCl, 37% KCl should be weighed out for analysis so that after the action of 25 ml of 0.1N $AgNO_3$ solution, excess of Ag^+ is back titrated with 5 ml of NH_4SCN solution? Given that 1 ml of NH_4SCN = 1.1 ml of $AgNO_3$.

$[AgNO_3 + NaSCN \rightarrow AgSCN + NaNO_3]$

Sol.

38. 10 g $CaCO_3$ were dissolved in 250 ml of 1 M HCl. What volume of 2 M KOH would be required to neutralise excess HCl ?

Sol.

39. A mixture of FeO and Fe_2O_3 is reacted with acidified $KMnO_4$ solution having a concentration of 0.2278 M, 100 ml of which was used. The solution was then titrated with Zn dust which converted Fe^{3+} of the solution to Fe^{2+}. The Fe^{2+} required 1000 ml of 0.13 M $K_2Cr_2O_7$ solution. Find the % of FeO & Fe_2O_3.

Sol.

40. 50 ml of a solution, containing 0.01 mole each Na_2CO_3, $NaHCO_3$ and NaOH was titrated with N-HCl. What will be the titre readings if

(a) only Ph is used as indicator.

(b) only MeOH is used as indicator from the beginning.

(c) MeOH is added after the first end point with Ph.

Sol.

41. 0.1 M $KMnO_4$ solution completely reacts with 0.05 M $FeSO_4$ solution under acidic conditions. The volume of $FeSO_4$ used is 25 ml. What volume of $KMnO_4$ was used?

Sol.

42. 20 g of a sample of $Ba(OH)_2$ is dissolved in 50 ml. of 0.1 N HCl solution. The excess of HCl was titrated with 0.1 N NaOH. The volume of NaOH used was 20cc. Calculate the % $Ba(OH)_2$ in the sample.

Sol.

43. 1 solution contains a mixture of Na_2CO_3 and NaOH. Using phenolphthalein as indicator. 25ml. of mixture required 19.5 ml. of 0.995 N HCl for the end point. With methyl orange. 25ml. of solution required 25 ml. of the same. HCl for the point. Calculate grams per litre of each substance in the mixture.

Sol.

44. 5.7 g of bleaching powder was suspended in 500 ml. of water. 25 ml. of this solution on treatment with KI in the presence of HCl liberated iodine which reacted with 24.35 ml. of N/10 $Na_2S_2O_3$. Calculate the % of 'available' chlorine in the bleaching powder.

Sol.

45. A solution containing 2.68×10^{-3} moles of A^{n+} ions requires 1.61×10^{-3} moles of MNO_4^- for the complete oxidation of A^{n+} to AO_3^- in acidic medium. What is the value of n?

Sol.

46. (i) What is the mas of sodium bromate and the solution necessary to prepare 85.5 mL of 0.672 N solution when the half cell reaction is $BrO_3^- + 56H^+ + 6e^- \rightarrow Br^- + 3H_2O$.

(ii) What would be the mass as well as molarity if the half cell reaction .

$2BrO_3^- + 12H^+ + 10e^- \rightarrow Br_2 + 6H_2O$

Sol.

47. A mixture of $H_2C_2O_4$ (oxalic acid) and $NaHC_2O_4$ was dissolved in water and the solution made upto one litre. Ten milliliters of the solution required 3.0 mL of 0.1 N sodium hydroxide solution for complete neutralization. In another experiment 10.0 mL of the same solution, in hot dilute sulphuric acid medium, required 4.0 mL of 0.1 N $KMnO_4$ solution for complete reaction. Calculate the masses of $H_2C_2O_4$ and $NaHC_2O_4$ in the mixture.

Sol.

48. A solution of 0.2 g of a compound containing Cu^{+2} and $C_2O_4^{-2}$ ions an titration with 0.02 M $KMnO_4$ in presence of H_2SO_4 consumes 22.6 mL of the oxidant. The resultant solution is neutralized with Na_2CO_3, acidified with dilute acetic acid and treated with excess KI. The liberated iodine requires 11.3 mL of 0.05 N $Na_2S_2O_3$ solution for complete reduction. Find out the mole ratio of Cu^{+2} to $C_2O_4^{-2}$ in the compound. Write down the balanced redox reactions involved in the above titration.

Sol.

49. A 2.0 g sample of a mixture containing sodium carbonate, sodium bicarbonate and sodium sulphate is heated till the evolution of CO_2 ceases. The volume of CO_2 at 750 mm Hg pressure and at 298 K is measured to be 123.9 ml. A 1.5 g of the sample requires 150 mL of M/10 HCl for complete neutralization. calculate the percentage composition of the components of the mixture.

Sol.

50. A solution contains Na_2CO_3 and $NaHCO_3$ 20 cm^3 of this solution requires 5.0 cm^3 of 0.1 M H_2SO_4 solution for neutralization using phenolphthalein as the indicator. Methylorange is then added when a further 5.0 cm^3 of 0.2 M H_2SO_4 was required. Calculate the masses of Na_2CO_3 and $NaHCO_3$ in 1 L of this solution.

Sol.

EXERCISE – IV PREVIOUS YEARS

LEVEL – I JEE MAIN

1. How many grams of H_2O_2 are required to convert 0.1 moles PbS to 0.1 moles $PbSO_4$ -

[AIEEE-2002]

(A) 12.8 g (B) 13.6 g

(D) 16 g (D) 3.4 g

Sol.

2. MnO_4^- is good oxidising agent in different medium changing to –

$MnO_4^- \longrightarrow Mn^{2+}$

$\longrightarrow MnO_4^{2-}$

$\longrightarrow MnO_2$

$\longrightarrow Mn_2O_3$

Changes in oxidation number respectively are – **[AIEEE-2002]**

(A) 1, 3, 4, 5 (B) 5, 4, 3, 2

(C) 5, 1, 3, 4 (D) 2, 6, 4, 3

Sol.

3. Oxidation number of Cl in $CaOCl_2$ (bleaching powder) is – **[AIEEE-2002]**

(A) Zero, since it contains Cl_2

(B) –1, since it contains Cl^-

(C) +1, since it contains ClO^-

(D) +1 and –1 since it contains ClO^- and Cl^-

Sol.

4. Which of the following is a redox-reaction-

[AIEEE-2002]

(A) $2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag$

(B) $BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$

(C) $N_2O_5 + H_2O \longrightarrow 2HNO_3$

(D) $AgNO_3 + KI \longrightarrow AgI + KNO_3$

Sol.

5. In the coordination compound, $K_4[Ni(CN)_4]$, the oxidation state of nickel is –**[AIEEE-2003]**

(A) +1 (B) +2

(C) –1 (D) 0

Sol.

6. What would happen when a solution of potassium chromate is treated with an dilute nitric acid ? **[AIEEE-2003]**

(A) CrO_4^{2-} is reduced to +3 state of Cr

(B) CrO_4^{2-} is oxidized to +7 state of Cr

(C) Cr^{3+} and $Cr_2O_7^{2-}$ are formed

(D) $Cr_2O_7^{2-}$ and H_2O are formed

Sol.

7. The oxidation state of Cr in $[Cr(NH_3)_4Cl_2]^+$ is – **[AIEEE-2005]**

(A) +2 (B) +3

(C) 0 (D) +1

Sol.

8. The oxidation state of chromium in the final product formed by the reaction between KI and acidified potassium dichromate solution is –**[AIEEE-2005]**

(A) +6 (B) +4

(C) +3 (D) +2

Sol.

9. Which of the following chemical reactions depicts the oxidizing behaviour of H_2SO_4 ?**[AIEEE 2006]**

(A) $Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O$

(B) $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$

(C) $2PCl_5 + H_2SO_4 \rightarrow 2POCl_3 + 2HCl + SO_2Cl_2$

(D) $2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O$

Sol.

LEVEL – II

JEE ADVANCED

1. Consider a titration of potassium dichromate solution with acidified Mohr's salt solution using diphenylamine as indicator. The number of moles of Mohr's salt required per mole of dichromate is

[JEE' 2007]

(A) 3 (B) 4

(C) 5 (D) 6

Sol.

2. Match the reactions in Column I with nature of the reactions / type of the products in Column II.

[JEE' 2007]

Column I	**Column II**
(A) $O_2^- \rightarrow O_2 + O_2^{2-}$	(P) Redox reaction
(B) $CrO_4^{2-} + H^+ \rightarrow$	(Q) One of the products has trigonal planar structure
(C) $MnO_4^- + NO_2^- + H^+ \rightarrow$	(R) dimeric bridged tetrahedral metal ion
(D) $NO_3^- + H_2SO_4 + Fe^{2+} \rightarrow$	(S) disproportionation

Sol.

3. White phosphorus on reaction with NaOH gives PH_3 as one of the products. This is a

[JEE 2008]

(A) dimerization reaction

(B) disproportionation reaction

(C) condensation reaction

(D) precipitation reaction

Sol.

4. The reaction of white phosphorus with aqueous NaOH gives phosphine along with another phosphorus containing compound. The reaction type; the oxidation states of phosphorus phosphine and the other product are respectively

[JEE 2012]

(A) redox reaction ; –3 and –5

(B) redox reaction ; + 3 and +5

(C) disproportionation reaction ; –3 and +5

(D) disproportionation reaction ; –3 and +3

Sol.

Paragraph for Question Nos. 5 and 6

Bleaching powder and bleach solution are produced on a large scale and used in several house hold products. The effectiveness of bleach solution is often measured by iodometry.

[JEE 2012]

5. 25 mL of household bleach solution was mixed with 30 mL of 0.50 M KI and 10 mL of 4 N acetic acid. In the titration of the liberated iodine, 48 mL of 0.25 N $Na_2S_2O_3$ was used to reach the end point. The molarity of the household bleach solution is

(A) 0.48 M (B) 0.96 M

(C) 0.24 M (D) 0.024 M

Sol.

6. Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxocacid is

(A) Cl_2O (B) Cl_2O_7

(C) ClO_2 (D) Cl_2O_6

Sol.

ANSWER-KEY

Answer Ex–I | OBJECTIVE PROBLEMS (JEE MAIN)

1. B	**2.** C	**3.** D	**4.** B	**5.** B	**6.** B	**7.** D	**8.** A
9. C	**10.** C	**11.** A	**12.** B	**13.** C	**14.** A	**15.** B	**16.** D
17. B	**18.** C	**19.** B	**20.** B	**21.** A	**22.** C	**23.** C	**24.** D
25. A	**26.** A	**27.** A	**28.** B	**29.** C	**30.** B	**31.** B	**32.** D
33. C	**34.** A	**35.** A	**36.** A	**37.** A	**38.** B	**39.** D	**40.** C
41. D	**42.** B	**43.** A	**44.** B	**45.** A	**46.** C	**47.** D	**48.** B
49. D	**50.** D						

Answer Ex–II | OBJECTIVE PROBLEMS (JEE ADVANCED)

1. A,C	**2.** A,C	**3.** A,B,C	**4.** C	**5.** A,B,C	**6.** A	**7.** A,B	**8.** A,B,C
9. A,B	**10.** A,C,D	**11.** A,C,D	**12.** B	**13.** A,C	**14.** B,C,D	**15.** A,B,C	**16.** A
17. B	**18.** C	**19.** D	**20.** B	**21.** A	**22.** C	**23.** D	**24.** A
25. D	**26.** C	**27.** A	**28.** B	**29.** C	**30.** A	**31.** C	**32.** B
33. B	**34.** A	**35.** 3g	**36.** n = 2	**37.** 100	**38.** A	**39.** A	**40.** D

41. D **42. D** **43.** D **44.** A→Q,B→P, C→S, D→R **45.** h,i,f,a,g,b,c,d,e **46.** D

47. C **48.** A **49.** B **50.** A

Answer Ex–III SUBJECTIVE PROBLEMS (JEE ADVANCED)

1. (a) $2KMnO_4 + 3H_2SO_4 + 5\,H_2O_2 \rightarrow$

$K_2SO_4 + 2MnSO_4 + 8\,H_2O + 5O_2$

(b) $2Cu^{2+} + 2I^- \rightarrow 2Cu^+ + I_2$

2. (i) $2CrI_3 + 27H_2O_2 + 10\,OH^- \rightarrow 2CrO_4^{2-} + 6IO_4^- + 32H_2O$

(ii) $258KOH + K_4Fe(CN)_6 + 61Ce(NO_3)_4 \rightarrow 61Ce(OH)_3 + Fe(OH)_3 + 36H_2O + 6K_2CO_3 + 250KNO_3$

3. (a) $2SbCl_3 + KIO_3 + 6HCl \rightarrow 2SbCl_5 + ICl + 3H_2O + KCl$

(b) $10FeC_2O_4 + 6KMnO_4 + 24H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + 20CO_2 + 6MnSO_4 + 3K_2SO_4 + 24H_2O$

4. $6FeCr_2O_4 + 12K_2CO_3 + 7KClO_3 \rightarrow 3Fe_2O_3 + 12K_2CrO_4 + 7KCl + 12CO_2$

5. $30Pb(N_3)_2 + 44Co(MnO_4)_3 \rightarrow 132MnO_2 + 44CoO + 180NO + 10Pb_3O_4$

6. $3KClO_3 + 3H_2SO_4 \rightarrow 3KHSO_4 + HClO_4 + 2ClO_2 + H_2O$

7. $5Br^- + BrO_3^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$

8. $24H_2S + 8Cr_2O_7^{2-} + 16H^+ \rightarrow 8Cr_2O_3 + 3S_8 + 32H_2O$

9. $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

10. $3Cu_2O + 14H^+ + 2NO_3^- \rightarrow 6Cu^{2+} + 2NO + 7H_2O$

11. $5[Fe(CN)_6]^{4-} + 188H^+ + 61MnO_4^- \rightarrow 5Fe^{3+} + 30CO_2 + 30NO_3^- + 61Mn^{2+} + 94H_2O$

12. $3C_2H_5OH + 2MnO_4^- + OH^- \rightarrow 3C_2H_3O^- + 2MnO_2(s) + 5H_2O$

13. $Cr_2O_7^{2-} + 3C_2H_4O + 8H^+ \rightarrow 3C_2H_4O_2 + 2Cr^{3+} + 4H_2O$

14. $8P + 3OH^- + 9H_2O \rightarrow 3H_2PO_4^- + 5PH_3$

15. $4S + 6OH^- \rightarrow 2S^{2-} + S_2O_3^{2-}$

16. $6Na_2S_2O_3 + 2KMnO_4 + 4H_2O \rightarrow 3Na_2S_4O_6 + 2MnO_2 + 2KOH + 6NaOH$

17. $10FeC_2O_4 + 6KMnO_4 + 24H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + 20CO_2 + 6MnSO_4 + 3K_2SO_4 + 24H_2O$

18. $C_2H_5OH + 4I_2 + 6OH^- \rightarrow CHI_3 + HCOO^- + 5H_2O + 5I^-$

19. KOH = 35%, $Ca(OH)_2$ = 65% **20.** V = 157.8 ml **21.** 20.72 % **22.** 200 mL

23. 0.424 gm; 0.21 gm **24.** 23.32 gm, 22.4 gm **25.** 0.06 gm; 0.0265 gm **26.** +3

27. zero **28.** V = 31.68 ml **29.** 0.588 N **30.** 337 mL

31. 41.53% **32.** 6.07 ≈ 6 **33.** 0.15 N **34.** 0.174g ; 3.48 % **35.** 1.406%

36. 90.1 % **37.** 0.1281 g **38.** V = 25 mL **39.** FeO = 13.34%; Fe_2O_3 = 86.66%

40. 20 ml ; 40 ml; 20 ml **41.** 2.5 ml **42.** 1.29 % **43.** 23.3, 24,4

44. 30.33 % **45.** 2 **46.** (i) 1.446 g, 0.112 M (ii) 1.735 g, 0.1344 M

47. $H_2C_2O_4$ = 0.9 g, $NaHC_2O_4$ = 1.12 g **48.** 1/2

49. $NaHCO_3$ = 42%, Na_2CO_3 = 26.5%, Na_2SO_4 = 31.5 % **50.** 5.3 g, 4.2g

Answer Ex–IV PREVIOUS YEARS PROBLEMS

LEVEL – I JEE MAIN

1. B **2.** C **3.** D **4.** A **5.** D **6.** D **7.** B **8.** C

9. D

LEVEL – II JEE ADVANCED

1. D **2.** (A) P, S ; (B) R ; (C) P, Q ; (D) P **3.** B 4. D **5.** C **6.** A